Mg–Zn–Y alloys with long-period stacking ordered structure: \textit{In vitro} assessments of biodegradation behavior

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A R T I C L E   I N F O

Article history:
Received 28 January 2013
Received in revised form 7 April 2013
Accepted 24 April 2013
Available online 3 May 2013

Keywords:
Degradable implants
Magnesium alloys
Long period stacking order
Corrosion
Simulated body fluid

A B S T R A C T

Using Dulbecco’s modified eagle medium (DMEM) with 10% fetal bovine serum (FBS) as simulated body fluid, degradation behavior of Mg100−x(ZnY2)x (1 ≤ x ≤ 3) alloy series with long period stacking order (LPSO) structures was investigated. As indicated, with increasing the volume fraction of LPSO phase, degradation rate of the alloys is accelerated. Further refining the grain size by microalloying with zirconium and warm extrusion has a significant effect to mitigate the degradation rate of the Mg96Zn2Y2 alloy. Time-dependent behavior during degradation of the magnesium alloys can be described using an exponential decay function of \( W_t = \exp(a + bt + ct^2) \), where \( W_t \) is normalized residual mass/volume of the alloy. A parameter named as degradation half-life period (\( t_{0.5} \)) is suggested to quantitatively assess the degradation rate. For the localized-corrosion controlled alloys, the \( t_{0.5} \) parameter physically scales with electrochemical response \( \Delta E \) which is a range between corrosion potential (\( E_{corr} \)) and pitting potential (\( E_{pt} \)). In comparison with conventional engineering magnesium alloys such as the AZ31, WE43, ZK60 and ZK60 alloys, extruded Mg96.8Zn1Y2Zr0.17 alloy with LPSO structure exhibits a good combination of high mechanical strength, lower biodegradation rate and good biocompatibility.

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1. Introduction

Over the past decade, magnesium and its alloys are considerably concerned as biomedical degradable implants, such as orthopedic devices and vascular stents [1–4]. It is motivated by a unique feature that Mg alloys are expected to be degradable and absorbable in human body, rather than permanently resident like titanium alloys and stainless steels. Then, from the perspective of orthopedic application, a second surgery is unnecessary to remove the temporary device for repair and fixation after the bone tissue has healed well. Moreover, Mg is an essential macro-element in human body. For a normal adult, daily intake of Mg is estimated to be about 400 mg, and excessive Mg can be excreted through the urine effectively [5,6]. As well known, Mg ion in the body has an effect to promote the mineral apposition rate and osteoblastic activity. It significantly stimulates the growth of new bone tissues, made the damaged bone healing more quickly [2].

As orthopedic implants, the desired material is required to possess a good combination of high strength and reasonable ductility. Meanwhile, a controllable degradation rate in physiological environment is also a key issue because over-fast degradation rates of implants bring about at least several problems. Firstly, hydrogen release as a corrosion product induced by degradation of Mg parts generates gas pockets [2–7]. The gas bubbles block the interaction between osteocytes and Mg implants, which interferes with the initial healing process of cortical bone, accompanied by callus formation [7]. Next, elevating the local pH value, caused by alkalization exceeding tolerable limit in the body, leads to an inflammation response. Thirdly, released excessive metal ions which are not absorbed through metabolism probably introduce additional long-term toxicity. Finally, the implants responsible for load bearing may lose their mechanical integrity prematurely, resulting in the failure of the implant surgery [8]. Consequently, control of the degradation rate in physiological environment remains a challenge for the clinical application of Mg alloys.

The degradation behavior of Mg alloys in the physiological environment not only depends on the metallurgical factors such as alloy composition and microstructure but also on the chemical nature of the media [5]. Metallurgical aspects deal with the impurity, alloying elements, and microstructure including the grain size and presence of second phase. As well known, impurity elements such as Fe, Ni, Cu and Co are able to accelerate corrosion rates by 10–100 folds, as long as their concentration exceeds the tolerance limit [10]. This is mainly attributed to their low solid-solubility limits in α-Mg and their roles as active cathodic sites [11,12]. From the view of alloying, the element Zn has the power to extend the tolerance limit of impurity elements, thus reducing the detrimental effect of impurities [10]. Element Y is able to stabilize the surface passive film formed on the Mg alloy [13,14]. It is of interest to note that the influence of grain size on corrosion behavior of Mg alloys is currently in debit. For the pure Mg with ultrafine grain size fabricated by equal channel angular pressing (ECAP), Birbilis et al. [15] showed that the corrosion rate

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http://dx.doi.org/10.1016/j.msec.2013.04.051
was mitigated by grain refinement, while Song et al. [16] presented the completely contrary tendency. Moreover, the effect of second phase on corrosion is believed to be dual sides, depending on its role played as a corrosion barrier or as a galvanic cathode [11].

To make the material selection for implants, the in vitro assessment of biodegradation behavior for Mg alloy in simulated body fluid (SBF) has been a conventional approach. However, a widely accepted method as the standard to evaluate the degradation rate of Mg alloys has not been well established so far. Due to the diversity of selected SBFs, it is clearly inadequate to make mutual comparisons using the data of degradation rates from different investigators [17]. Currently, the conventional recipe of SBFs includes the Hank’s solution, phosphate buffer solution (PBS) and c-SBF. These media contain similar concentrations of inorganic salt ions, but in the absence of amino acid and protein which are major biochemical components in the human body. As indicated, amino acids and proteins have great effects on the degradation behavior of Mg alloys [18,19]. Thus, to mimic the actual conditions in the body, it is obviously necessary to incorporate the amino acids and proteins in the fluids. On the other hand, degradation rates estimated in terms of in vivo implant and in vitro approaches are not completely in parallel and consistent. Witte et al. [20] illustrated that the in vitro degradation rate of AZ91D alloy is lower than that of LAE442, while in vivo assessment presented the contrary trend. Therefore, it should be careful to claim the difference in degradation rate between alloys.

Recently, ternary Mg–Zn–Y alloys with long period stacking ordered (LPSO) phase are revealed to possess high strength and usable ductility [21,22]. In the sense of biocompatibility, Zn has a large influence factors on biodegradation behavior of Mg alloys [18,19]. Thus, to mimic the actual conditions in the body, it is obviously necessary to incorporate the amino acids and proteins in the fluids. On the other hand, degradation rates estimated in terms of in vivo implant and in vitro approaches are not completely in parallel and consistent. Witte et al. [20] illustrated that the in vitro degradation rate of AZ91D alloy is lower than that of LAE442, while in vivo assessment presented the contrary trend. Therefore, it should be careful to claim the difference in degradation rate between alloys.

As-cast ingots of Mg–Zn–Y(Zr) alloys were fabricated by induction-melting using pure Mg (99.99%) and Zn (99.999%) with high purity, and the medium alloys of Mg–30%Y weight percentage (wt.%) and Mg–30%Zr (wt.%). For the warm-extruded alloys, Mg96.83Zn1Y2Zr0.17 ingots were prepared using an electrical resistance furnace. The warm-extruded conditions are presented elsewhere [25]. Three commercial alloys, WE43 (Mg–4Y–3RE–0.6Zr), ZK60 (Mg–6Zn–0.6Zr) and ZK60 (Mg–6Zn–0.3Ca), are selected in the as-cast state. They were smelted in electrical resistance furnace and cast into a steel mold with a diameter of 50 mm cavity. The AZ31 (Mg–3Al–1Zn–0.3Mn) alloy was taken from the extruded bar of 15 mm diameter, extruded at 623 K and with a ratio of 10:1. Concentration of impurities in the alloys was analyzed using Magix Pro PW2440 (Philips, the Netherlands) X-ray Fluorescence Spectrometer (XRF).

Rectangular samples used for weight loss tests during immersion in medium were machined from as-cast ingots or extruded rods, in a dimension of 10 mm × 10 mm × 2 mm. Specimens for electrochemical measurements were embedded in epoxy resin with a top surface exposed area of 1 cm². All samples were ground with 2000 grit SiC papers and then ultrasonically cleaned in ethanol for 5 min and dried in air.

2.2. Immersion testing

A conventional cell culture medium, Dulbecco’s modified eagle medium (DMEM, Invitrogen Corporation) with a recipe of 4.5 g/L glucose and 110 mg/L sodium pyruvate plus 10% fetal bovine serum (FBS) was selected as SBF. Meanwhile, an atmosphere of 5% CO₂ and 21% O₂ was maintained in CO₂ incubator (BC-J60S, Boxun, China), with 37 °C and 95% relative humidity to mimic physiological environment. The pH value of the solution was adjusted to 7.4 before testing with a volume of 50 ml for each test. The solution was refreshed with an interval of every two days to minimize biochemical variation, and its pH value was measured during the initial two days. After soaking to designed time, the samples were ultrasonically cleaned with 20% chromic acid for 5 min to remove the corrosion products, and then washed with distilled water and dried in air. The weighted mass changes of sample was measured after soaking for 21 days with an accuracy of 0.1 mg. The degradation rate of samples was defined as follows:

\[
W_R = \frac{W'}{W} \times 100\% 
\]

where \(W_R\) is the normalized residual mass, and \(W\) and \(W'\) represent the sample masses before and after immersion, respectively.

Surface morphologies of the degraded samples were characterized using Quanta 600 (FEI, the Netherlands) scanning electron microscopy (SEM).

2.3. Electrochemical measurements

Electrochemical measurements were also performed in a solution of DMEM with 10% FBS in CO₂ incubator. An electrochemical workstation of EG&G PAR 2273 was used to measure the potentiodynamic polarization, potentiostatic polarization and electrochemical impedance spectroscopy (EIS). A standard three electrode configuration was used, with a saturated calomel electrode (SCE) as reference electrode. A platinum plate and the sample were used as the counter electrode and working electrode, respectively. After recording open circuit potential (OCP) for 1h, potentiodynamic polarization tests were conducted at a scanning rate of 0.3 mV/s. After immersion for 1 h, the EIS were measured at the OCP with AC amplitude of 10 mV over a frequency range from 10 mHz to 100 kHz. Data of impedance spectra was fitted using the ZsimWin 3.2 software.

3. Results

3.1. Effect of LPSO phase fraction on the degradation behavior

Microstructure of as-cast Mg_{61.00–3x}Zn_{1.00}Y_{2}Zr_{0.17} (1 ≤ x ≤ 3 at.%) alloys was characterized in our previous work [25]. The alloys consist of the
α-Mg phase and 18R LPSO phase. With increasing the x in the alloys, grain size of α-Mg dendrite decreases from 150 μm at x = 1 to 80 μm at x = 3. Meanwhile, volume fraction of LPSO phase at the composition of x = 1, 2 and 3 is estimated to be 25, 48 and 66 vol.% respectively.

The pH value of the soaking solution was measured in immersion for the first 48 h before the medium was refreshed. Fig. 1 displays the variation of pH value with extending immersion time for the three Mg100−x(Zn1Y2)x alloys. As indicated, the pH values are drastically elevated during immersion for the first 24 h, and subsequently, the increased trend tend towards a steady state gradually. Increasing the x induces an elevation of pH values. After immersion for 48 h, the pH value of the alloy at x = 1, 2 and 3 is determined as 7.6, 7.8 and 8.2, respectively. Alkalization of the solution is evident as the time extends, which is caused by dissolution of the Mg ion from the alloys. In other words, it is indicated that increasing the volume fraction of LPSO phase in the alloys accelerates the degradation.

Fig. 1. The pH value of the soaking solution as a function of immersion time for three as-cast Mg100−x(Zn1Y2)x (x = 1, 2, 3) alloys.

Fig. 2(a)–(d) illustrates global appearance of partially-degraded samples of Mg100−x(Zn1Y2)x alloys subjected to immersion with extending periods. The localized corrosion is clearly visible after immersion periods even less than 1 day. Preferred sites for localized corrosion appear at the edges of the samples. This means that with extending the immersion time, mode of corrosion damage translates from uniform corrosion to localized corrosion. For the alloy at x = 1, onset-time of pitting approximately starts at 5 days of immersion. Similarly, the onset-time of pitting for the alloys at x = 2 and at x = 3 is around 2 days and 1 day, respectively. Evidently, increasing the volume fraction of LPSO phase made localized corrosion more susceptive.

Fig. 2. Global appearance of partially-degraded Mg100−x(Zn1Y2)x alloys after immersion for several periods. (a) x = 1, (c) x = 2 and (d) x = 3 soaked for 3 days, as well as (b) x = 1 soaked for 7 days.

Fig. 3(a)–(d) shows SEM images of partially-degraded Mg100−x(Zn1Y2)x alloys. As seen in Fig. 3(a), the surface of Mg97Zn1Y2 (x = 1) sample is covered with intact and compact films after immersion for 3 days. The LPSO phase with lighter contrast is inserted in the surface layer. Cracks formed in the surface layer are generated due to drying-induced dehydration. The surface layer was broken after immersion for 7 days. Subsequently, loose and porous corrosion products were left over at the corroded sites. For the alloys at x = 2 and at x = 3, porous corrosion products emerge at 3 days of immersion.

Fig. 4(a) shows a plot of normalized residual mass (WR) against immersion periods of the three alloys. With extending the immersion time, the WR decreases, with a monotonically dramatic drop with increasing the x or volume fraction of LPSO phase. It also illustrates...
that the degradation rate is accelerated with the increase of x. Based on these data, the trend of mass decay with time (t) extension is fitted using an exponential function of
\[ W(t) = W_0 \exp(a + bt + ct^2) \], which is an empirical formula, presented as the curves in Fig. 4(a). Here, we define the time point at 50% of weighted mass loss as degradation half-life period \( t_{0.5} \), which is obtained by the fitting equation if the mass loss determined from the immersion tests is less than 50% of the initial mass. As a result, it is indicated that with increasing the x in the alloys, the \( t_{0.5} \) is significantly shortened, from about 43 days at \( x = 1 \) down to 4 days at \( x = 3 \).

Fig. 5(a) shows potentiodynamic polarization curves of the three Mg–Zn–Y alloys. With increasing the x, cathodic parts of the curves shift to the side of low current density, which means that the cathodic reaction of hydrogen evolution is restrained. From anodic parts of the curves, knee points appear at a certain potential, as marked by arrows. Below the knee points, anodic current density increases gently, while current density rapidly increases over the point. Such an increase of current density results from the local breakdown of surface passive layer, which corresponds to a potential named as breakdown potentials \( E_{br} \), as seen in Fig. 5(a). As noted, the alloys manifest pseudopassivation behavior over a range between corrosion potential \( E_{corr} \) and \( E_{pt} \). This potential range is expressed as \( \Delta E \), and reflects stability of passive film on the surface. Electrochemical parameters obtained from potentiodynamic polarization for the three alloys are listed in Table 1. The current density, \( i_{corr} \), is calculated with Tafel extrapolation method, which associates with the uniform corrosion rate because no breaking of surface layer happens in the Tafel region. With increasing the x, the \( i_{corr} \) decreases. It reflects that the degradation rate of the alloy is mitigated at the stage of uniform corrosion. The reduction of the \( \Delta E \) with increasing the x indicates a fact that localized corrosion easily happens, which is consistent with the performance of soaked samples, as shown in Fig. 2.

Fig. 6(a) and (b) displays an electrochemical impedance spectrum (EIS) of \( \text{Mg}_{100-x}(\text{Zn}_x\text{Y}_2) \alpha \) alloys. As seen in Fig. 6(a), with increasing the x, the impedance (|Z|) increases, reflecting an enhancement of corrosion resistance of the alloy. From the phase degree curves in Bode diagrams as shown in Fig. 6(a), two time constants are deduced. According to the two capacitive loops in Nyquist diagrams as shown in Fig. 6(b), time constants at high and low frequencies are obtained. With increasing the x, capacitive loop extends to a larger range, which is consistent with the case as seen in Fig. 6(a). This means that protection ability of the surface layer is improved. Based on the rule of minimum value of circuit components [26], the impedance data are fitted using an equivalent circuit with two time constants, as shown in Fig. 6(c). In the circuit, the \( R_q \) represents the solution resistance irrespective of the electrode process, whereas the \( R_s \) is a resistance to charge transfer, parallel to the double layer capacity which is a constant-phase-element (CPE). \( R_2 \) and C refer to the resistance and capacity of the surface layer, respectively. The parameters obtained from fitting are listed in Table 2. As noticed, the alloy at \( x = 2 \) shows the largest film resistance with \( R_s = 3767 \ \Omega \ cm^2 \), while the alloy at \( x = 3 \) is remarkably different from the two rest alloys. Such a change is attributed to the microstructure transition of the matrix phase in the alloy from \( \alpha \)-Mg to LPSO phase at \( x = 3 \).

3.2. Effects of Zr-microalloyed and warm-extruded on the degradation behavior

Microstructure of as-cast and as-extruded \( \text{Mg}_{96.83}\text{Zn}_1\text{Y}_2\text{Zr}_{0.17} \) alloys was presented elsewhere [25]. For the alloy microalloyed with Zr, equiaxed grains of \( \alpha \)-Mg formed in size of about 30 \( \mu \)m, together with the reticular LPSO phase distributed at grain boundaries of \( \alpha \)-Mg grains. In the warm-extruded alloy, grain size of \( \alpha \)-Mg was further refined down to 15 \( \mu \)m, whereas the LPSO phase aligns along the extrusion direction.

Fig. 7(a)–(d) shows global appearance of as-cast and as-extruded \( \text{Mg}_{96.83}\text{Zn}_1\text{Y}_2\text{Zr}_{0.17} \) samples immersed for 7 and 14 days. In both cases, localized corrosion took place. In contrast to Zr-free alloys, Zr-containing alloys possess higher resistance to localized corrosion, with an onset-time of pitting at 10 days. Subjected to extrusion
deformation, the corrosion behavior of the alloy is substantially comparable to the as-cast state, showing the onset-time of pitting at 11 days. It indicates that grain refinement induced by Zr incorporation significantly improves the corrosion resistance. Fig. 4(b) displays the normalized residual mass of as-cast and as-extruded Mg_{60.63}Zn_{1}Y_{2}Zr_{0.17} alloys during immersion. The $W_R$ as a function of immersion period were fitted using the equation of $W_R = \exp(a + bt + ct^2)$ as well. In contrast to Zr-free alloys, Zr-containing alloys exhibit a longer degradation half-life period. The $t_{0.5}$ of as-cast and as-extruded alloys is determined at 56 days and 68 days, respectively. This means that the grain refinement induced by Zr micro-alloying plays a remarkable role to mitigate the degradation rate, but further extrusion deformation only provides a slight improvement on the degradation mitigation.

Fig. 5(b) shows potentiodynamic polarization curves of as-cast and as-extruded Mg_{66.83}Zn_{1}Y_{2}Zr_{0.17} alloys. Measured electrochemical parameters of the alloys at two processing conditions are listed in Table 1 as well for a comparison. It is indicated that corrosion potentials of Zr-containing alloys are lower than those of Zr-free alloy. From the anodic parts of the curves, breakdown potentials, $E_{bpt}$, appear at −1.417 V for as-cast alloy and −1.418 V for as-extruded alloy. In contrast to the Zr-free alloy, Zr-containing alloys have a much higher $AE$, which means that the surface layer of Zr-containing alloy is more stable, namely, that pitting resistance was enhanced. For the extruded alloy, the cathodic part of the curve shifts to the low current density side, indicating that hydrogen evolution reaction is restrained. As a representative, the potential caused by the breakdown of the surface layer was confirmed also by potentiostatic polarization for the extruded alloy, as shown in Fig. 5(c). The curves marked as A and B in Fig. 5(b) represent the scanning potentials just below and above $E_{bpt}$. With extending the scanning time, current density in curve A remains unchanged at a value near zero, while the current density in curve B is elevated to a value much larger than that in curve A. It is evident that the surface layer was broken above the $E_{bpt}$, no longer maintaining the protection function.

3.3. Comparison with several typical commercial Mg alloys

Fig. 8(a)-(d) shows global appearance of partially-degraded AZ31, WE43, ZK60 and ZX60 alloys after immersion for 21 days. Only uniform corrosion takes place in the AZ31 and WE43 alloys after immersion for 21 days, without a visible localized corrosion. However, a localized corrosion happens in the ZK60 and ZX60 alloys. Their onset-time of pitting appears at around 4 days. As shown in Fig. 8(a) and (b), the corrosion mode of uniform corrosion maintains until immersion to 21 days in the AZ31 and WE43 alloys. Fig. 9(a)-(d) shows SEM images taken from the sample surfaces of partially-degraded AZ31, WE43, ZK60 and ZX60 alloys after immersion for 21 days. As seen in Fig. 9(a) and (b), the surface layers in the AZ31 and WE43 alloys are intact and dense, indicating the absence of localized corrosion after immersion even for 21 days. As seen in Fig. 9(a), no second phase is present in the AZ31 alloy besides a uniform surface layer. The phase with lighter contrast shown in Fig. 9(c) and (d) are identified as the trace sites of localized corrosion. The particles and strips with lighter contrast shown in Fig. 9(c) and (d) are identified as pure Zn, which are precipitated due to the alloy dissolution.

Fig. 5(d) shows potentiodynamic polarization curves of the AZ31, WE43, ZK60 and ZX60 alloys. Measured electrochemical parameters...
of these alloys are listed in Table 1 also for a comparison. In all cases, the \(E_p\) appears at anodic parts of each curve. Corrosion potential of the AZ31, ZK60, and ZX60 alloys is comparative, while WE43 alloy possesses a corrosion potential lower than three rest alloys. Current density of these alloys is maintained at the same magnitude. The pseudo-passivation region, \(\Delta E\), is determined as 145, 227, 91 and 116 mV for the AZ31, WE43, ZK60 and ZX60 alloys, respectively. It further proves that stability of the surface passive layer increases in the following order: ZK60, ZX60, AZ31 and WE43.

### 4. Discussion

#### 4.1. Degradation process of LPSO-containing alloys

As it is well characterized, microstructures of LPSO-containing Mg–Zn–Y alloys consist of two phases, the \(\alpha\)-Mg and LPSO phases [25]. It implies that localized corrosion induced by a galvanic couple effect is probably inevitable. With high content of alloying elements, LPSO phase in the alloy plays a role of local cathode in the medium during degradation, while the \(\alpha\)-Mg phase adjacent to the LPSO phase acts as an anode and is preferentially dissolved.

As indicated in Section 3.1, the degradation process of LPSO-containing alloys in the solution is dominated by two pieces of mechanism: uniform corrosion and localized corrosion at different stages. At the initial period of immersion, the \(\alpha\)-Mg phase encounters an anodic dissolution, accompanied by the formation of \(\text{Mg(OH)}_2\) film in the alloy surface. It is chemically described as the following reactions.

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2e\text{(anodic reaction)} \tag{2}
\]

\[
2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \text{(cathodic reaction)} \tag{3}
\]

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2. \tag{4}
\]

Under the simulated physiological condition, spontaneously passivated oxide film in the surface provides temporary corrosion resistance of the alloy matrix. It gives rise to the uniform corrosion that
which are preferential sites for galvanic corrosion. Thereafter, degradation of the alloys is mainly controlled by a localized corrosion instead of a uniform corrosion.

In the Mg_{100-3x}(Zn_{1}Y_{2})_{x} (1 \leq x \leq 3) series alloys, increasing the x in the alloys brings about drastic increase in the volume fraction of the LPSO phase. Evidently, LPSO-containing alloys are favorable to galvanic corrosion, namely, more susceptible to localized corrosion. It was indicated by the short onset-time of pitting and reduced ΔE value. Fig. 10(a) displays a plot of onset-time of pitting against ΔE. As seen in Fig. 10(a), extended onset-time of pitting is approximately increased linearly with ΔE, with a correlation coefficient of 0.96.

In the two stages with different mechanisms, the degradation behavior of LPSO-containing alloys is obviously distinct. Firstly, with increasing the x, semi-continuously distributed LPSO phase becomes more continuous in morphology. At the stage of uniform corrosion, dissolution of α-Mg phase is retarded owing to the presence of LPSO phase. Thus, the alloys with higher volume fraction of LPSO phase exhibit better corrosion resistance. Next, as the pitting corrosion occurs subsequently, a galvanic couple effect of LPSO phase determines the degradation process. It results in that degradation rates of the alloys with higher volume fraction of LPSO phase are accelerated.

4.2. Influence of metallurgical factors on degradation

Considering the deleterious effect on corrosion, concentrations of impurity elements such as Cu and Fe in the Mg_{100-3x}(Zn_{1}Y_{2})_{x} alloys are measured. As shown in Fig. 11, increasing the x in the alloys does not change the Cu content; which maintains at a level much lower than the tolerance limits of 0.03% (300 ppm) [10]. On the contrary, the Fe content in the alloys is sharply elevated, reaching to a level higher than the tolerance limits of 0.017% in all three alloys [10]. In addition, the Ni content in all three alloys is less than 0.001% (not shown here), far below the tolerance limits of Ni in Mg alloys [10]. As a result, influence of Cu and Ni elements as impurities on degradation of the investigated alloys is negligible, but acceleration of degradation rate caused by Fe impurity is evident. It implies that Fe impurity also partially contributes to the fast degradation rate of the alloys with a high volume fraction of LPSO phase. Chemical analysis indicates that the Fe impurity is brought mainly from the starting medium Mg-Y alloys with the Fe content of 0.09%.

With much higher concentration of alloying elements with respect to the α-Mg phase, as usual, the corrosion potential of the second phase in the alloy is higher than that of α-Mg phase, performing a better corrosion resistance. Thus, the second phase such as intermetallics usually acts as a cathode coupled with α-Mg phase, which yields a dual effect on the corrosion behavior of Mg alloys [10]. The fraction and distribution of the second phase determine its function as a corrosion barrier or as a galvanic cathode for accelerating corrosion. As discussed in Section 4.1, with increasing the volume fraction of the LPSO phase, corrosion resistance of alloys is enhanced due to the protection function of the LPSO phase. In contrast, degradation rates are accelerated by a galvanic couple effect of the LPSO phase in the stage of localized corrosion.

In comparison with the Mg_{97}Zn_{1}Y_{2} alloy, the grain size of as-cast Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloy is refined from 150 μm to 30 μm by virtue of microalloying with Zr. Morphology of the LPSO phase becomes more continuous and reticular. The degradation rate of a 2r-containing alloy was significantly mitigated, as indicated by an extension of onset-time of pitting and degradation half-life period (see Fig. 4(b)]. It indicates that grain refinement is a valid approach to mitigate the degradation rate of LPSO-containing alloys. In fact, our finding is consistent with the results shown by Birbilis et al. [15], in which increasing the grain boundary density gave rise to a reduction of corrosion current density for the pure Mg with refined grains by ECAP processing. In addition, Lzumi et al. [27] revealed that the corrosion rate of

![Graph](image)

**Fig. 6.** Electrochemical impedance spectrum measured in DMEM + FBS medium for Mg_{100-3x}(Zn_{1}Y_{2})_{x} (x = 1, 2, 3) alloys after immersion for 1 h. (a) Bode diagrams, (b) Nyquist diagrams, and (c) equivalent circuit for fitting Nyquist diagrams.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Equivalent circuit parameters of as-cast Mg_{100-3x}(Zn_{1}Y_{2})_{x} (x = 1, 2, 3) alloys fitted with Nyquist diagrams.</th>
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<tbody>
<tr>
<td>Alloy</td>
<td>R_0 (Ω cm²)</td>
</tr>
<tr>
<td>x = 1</td>
<td>15</td>
</tr>
<tr>
<td>x = 2</td>
<td>21</td>
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<tr>
<td>x = 3</td>
<td>20</td>
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Fig. 7. Global appearance of partially-degraded Mg$_{96.83}$Zn$_1$Y$_2$Zr$_{0.17}$ alloys after immersion for (a), (c) 7 days and (b), (d) 14 days. (a) and (b) in as-cast state. (c) and (d) in as-extruded state.

Fig. 8. Global appearance of partially-degraded commercial alloys after immersion for 21 days. (a) AZ31, (b) WE43, (c) ZK60 and (d) ZX60.
Mg–Zn–Y alloys can be reduced through grain refinement by rapid-solidification. For the warm-extruded alloys, the degradation rate of Mg$_{96.83}$Zn$_1$Y$_2$Zr$_{0.17}$ alloy is mitigated, showing an extension of degradation half-life period. Ben-Hamu et al. [28] showed that the corrosion rate of an AZ31 alloy can be slowed down by conventional extrusion, due to the effect of grain refinement. In contrast, Zhang et al. [29] displayed that the corrosion rate of as-extruded AZ91 is higher than that of as-cast one, and the corrosion rate for the transversal section is higher than that for the longitudinal section. For the extruded AZ80 alloy, Ben-Haroush et al. [30] revealed that the rearrangement of the second phase results in a decrease of the corrosion resistance. In terms of these findings, a conclusion can be drawn that the extrusion-deformation effects on the corrosion behavior is dependent

Fig. 9. SEM images taken from surface of partially-degraded commercial alloys after immersion for 21 days. (a) AZ31, (b) WE43, (c) ZK60 and (d) ZX60.

Mg–Zn–Y alloys can be reduced through grain refinement by rapid-solidification. For the warm-extruded alloys, the degradation rate of Mg$_{96.83}$Zn$_1$Y$_2$Zr$_{0.17}$ alloy is mitigated, showing an extension of degradation half-life period. Ben-Hamu et al. [28] showed that the corrosion rate of an AZ31 alloy can be slowed down by conventional extrusion, due to the effect of grain refinement. In contrast, Zhang et al. [29] displayed that the corrosion rate of as-extruded AZ91 is higher than that of as-cast one, and the corrosion rate for the transversal section is higher than that for the longitudinal section. For the extruded AZ80 alloy, Ben-Haroush et al. [30] revealed that the rearrangement of the second phase results in a decrease of the corrosion resistance. In terms of these findings, a conclusion can be drawn that the extrusion-deformation effects on the corrosion behavior is dependent

Fig. 10. Plots of the potential range between corrosion potential and pitting potential ($\Delta E$) against (a) onset-time of pitting and (b) degradation half-life period. The alphabet letters C and E in the legend represent as-cast and as-extruded states, respectively.

Fig. 11. Concentration of Fe and Cu as impurity elements in as-cast Mg$_{100-3x}$Zn$_x$Y$_2$ alloys ($x = 1, 2, 3$) alloys.
of two issues, grain refinement and morphology of the second phase. In the current work, the degradation behavior of the as-extruded Mg0.81Zn0.17Y0.17 alloy is mainly dominated by the effect of grain refinement, which plays a role of mitigating the degradation.

In the present work, commercial AZ31 and WE43 alloys only present uniform corrosion during immersion in simulated physiological conditions, whereas the ZK60 and ZX60 alloys manifest a degradation behavior similar to the LPSO-containing alloys. Microstructure in the AZ31 shows a single α-Mg phase with a negligible galvanic couple effect. Such a homogeneous microstructure is relatively insensitive to pitting corrosion. In the WE43 alloy, its microstructure contains the α-Mg matrix and eutectic colony distributed at grain boundaries. Meanwhile, Zr- and Fe-rich dispersions are not detectable on the surface, as indicated by Kalb et al. [31]. Galvanic corrosion between Zr-rich dispersions is absent, and the corrosion potential of eutectic phases is only slightly higher than that of α-Mg matrix [31,32]. Therefore, localized corrosion does not take place during the entire period of immersion. In the ZK60 and ZX60 alloys, second phases are noble with respect to the matrix, then acting as cathodes to accelerate the dissolution of α-Mg phase.

Based on these findings, several approaches to mitigate the degradation rate of Mg alloys in a physiological environment are suggested, including the reduction of impurity content, grain refinement, optimization of the morphology and distribution of the second phase and selection of adequate alloying elements.

4.3. Assessment of degradation rates

Currently, degradation rates determined by in vitro and in vivo assessment for the Mg alloys present a significant inconsistency. As indicated by Witte et al. [20], the degradation rate estimated from microcomputerized tomography (μ-CT) of in vivo implant is about one order of magnitude lower than that in vitro assessment with electrochemical test in solution of artificial sea water. In comparison with the alloys with different compositions, degradation rate under an in vivo condition of AZ91D is much faster than that of LAE442, but the opposite tendency appeared under an in vitro scenario [20]. Li et al. [3] also showed that for a given alloy, degradation rate assessed by in vitro electrochemical tests in c-SBF was much faster than that estimated from in vivo weight loss of implants. On the contrary, Zhang et al. [33] presented the opposite results. The remarkable inconsistency between in vitro and in vivo assessment is mainly due to the complexity of the real physiological conditions. For instance, owing to the metabolism in organism, the physiological environment is dynamic with the exchange of body fluid and nutrition. As a result, it is difficult to simulate the real world in the body only in terms of in vitro assessment. Currently-used methods to assess the degradation behavior of Mg alloys are not fully satisfactory [34]. At least, it is necessary to incorporate the effects of amino acid and protein simulated body fluids for the assessment. As indicated, amino acid has an effect to promote the degradation through chelating with metal ions and inhibiting the formation of protective surface [19]. The influence of protein is dependent on alloy composition [35]. AZ91 alloy with high Al content showed a lower degradation rate in protein-containing solutions [36], which is also the case of Mg–Ca binary alloy [37], because the protein can be adsorbed on the oxide layers, then to enhance corrosion resistance of alloys. For the AZ31 alloy with low Al content, adding protein in the fluid had little effect on the electrochemical behavior [38]. In the case of pure Mg and LAE442 alloy, adding protein in the fluid promotes the degradation [38]. In the present work, the DMEM + FBS solution was used as a simulated physiological condition for in vitro assessment, which is expected to make the tendency of in vitro degradation more parallel to the in vivo cases.

As a matter of fact, the degradation behavior of Mg alloys either in vitro or in vivo is directly operated by a corrosion mechanism. However, due to the complexity of the corrosion processes, the corrosion rate is time-dependent, namely, which varies with extending service time. As a result, it has been a challenge to find adequate parameter to characterize the degradation rates. In this work, we suggest to use degradation half-life period (t0.5) of mass/volume loss in medium soaking as a parameter for comparison. This parameter provides a comparative message for different alloys degraded either in vitro or in vivo. On the other hand, as revealed in most cases, degradation rate of the implants is mainly controlled by localized corrosion. In the sense of electrochemistry, the ΔE is an indicator of susceptibility to pitting corrosion. Then, it is expected that the t0.5 physically scales with the ΔE. Fig. 10(b) shows a plot of t0.5 versus ΔE for six investigated Mg alloys. As indicated, the interplay between t0.5 and ΔE presents a good linear relationship with a correlation coefficient of 0.81, but the AZ31 and WE43 alloys clearly stand out. This is because these two alloys do not encounter localized corrosion in the current situations, then the ΔE is inadequate to characterize the whole picture of the degradation behavior.

4.4. Comparison of LPSO-containing alloys with several typical Mg alloys

As biodegradable implants, mechanical properties, degradation behavior and biocompatibility of Mg alloys are critical issues for alloy design. In many cases, approach of strengthening the alloy is in conflict to reducing the degradation rate and keeping biocompatibility. In order to compromise the mechanical properties and degradation rate, Fig. 12 shows a plot of the t0.5 against the α0.2 for the investigated alloys. As seen in Fig. 12, the AZ31 and WE43 alloys manifest a good combination of higher strength and longer degradation half-life period in comparison with our LPSO-containing Mg0.81Zn0.17Y0.17 alloys. Nevertheless, from the view of biocompatibility, Al and rare earth elements are not selected as first priority for alloy design used as implants [39]. In this sense, Mg–Zn–V alloys with LPSO phase seem to be the more interesting candidate. Further work will focus on the reduction of impurity contents in the alloys and optimization of extrusion variables for microstructure homogeneity.

5. Conclusions

(i) Under simulated physiological conditions, the in vitro degradation process of as-cast Mg0.81Zn0.17Y0.17 (1 ≤ x ≤ 3) alloys with long period stacking order (LPSO) structures is mainly controlled by localized corrosion. With increasing the volume fraction of LPSO phase, the degradation rate is accelerated due to a galvanic couple effect. On further microalloying with zirconium together with warm extrusion, the degradation

![Fig. 12. Schematic diagram of optimization for tensile yield strength and degradation half-life period for the investigated Mg alloys. The alphabet letters C and E in the legend represent as-cast and as-extruded states, respectively.](image-url)
rate of Zr-containing alloy, Mg96.83Zn1Y2Zr0.17, is significantly mitigated in contrast to the Zr-free alloy and as-cast state, due to the effect of grain refinement.

(ii) In in vitro conditions, degradation processes of the Mg alloys are time-dependent, and can be described using an exponential decay function of \( W_R = \exp(a + bt + ct^2) \), where \( W_R \) is normalized residual mass/volume of the alloy or implant. We define the time point at 50% of mass/volume loss as degradation half-life period (\( t_{0.5} \)). This \( t_{0.5} \) parameter provides a feasibility to make a quantitative comparison of the degradation rate with various alloys. For the localized-corrosion controlled alloys, the \( t_{0.5} \) parameter physically scales with electrochemical response \( \Delta E \) that is a range between corrosion potential \( (E_{corr}) \) and pitting potential \( (E_{pt}) \).

(iii) In comparison with conventional engineering magnesium alloys such as the AZ31, WE43, ZK60 and ZK60 alloys, warm-extruded Mg96.83Zn1Y2Zr0.17 alloy with LPSO structure exhibits a good combination in high mechanical strength and lower degradation rate. It is promising as a candidate material for biodegradable orthopedic implants.

Acknowledgments

The authors gratefully acknowledge Prof. K. Yang and Prof. R. S. Chen for providing the samples of commercial magnesium alloys. This work was supported by the National Natural Science Foundation of China under Grant No. 51001099.

References