



Effect of solid solution treatment on in vitro degradation rate of as-extruded Mg–Zn–Ag alloys

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Abstract: The degradation behaviors of the as-extruded and solution treated Mg–3Zn– x Ag ($x=0, 1, 3$, mass fraction, %) alloys, as well as as-extruded pure Mg, have been investigated by immersion tests in simulated body fluid (SBF) at 37 °C. The as-extruded Mg–Zn(–Ag) alloys contained Mg₅₁Zn₂₀ and Ag₁₇Mg₅₄. While the quasi-single phase Mg–Zn(–Ag) alloys were obtained by solution treatment at 400 °C for 8 h. The quasi-single phase Mg–Zn(–Ag) alloys showed lower degradation rate and more homogeneous degradation than corresponding as-extruded Mg alloys. Degradation rate of solid-solution treated Mg–3Zn–1Ag and Mg–3Zn–3Ag was approximately half that of corresponding as-extruded Mg alloy. Moreover, the degradation rate of solid-solution treated Mg–3Zn and Mg–3Zn–1Ag was equivalent to that of as-extruded pure Mg. However, heterogeneous degradation also occurred in quasi-single phase Mg–Zn–Ag alloys, compared to pure Mg. So, preparing complete single-phase Mg alloys could be a potential and feasible way to improve the corrosion resistance.

Key words: biodegradable Mg alloy; Mg–Zn–Ag alloy; solution treatment; corrosion resistance

1 Introduction

The bio-degradability and good bio-compatibility make Mg and its alloys attractive as biodegradable materials [1]. In the past decades, the commercial Mg alloys, such as AZ31, AZ91 and WE43 [2–5], were the popular biodegradable metallic alloys. Meanwhile, novel Mg alloys containing Zn, Ca, Sr and/or rare earth elements had been developed as biodegradable Mg alloys [6–10] by different preparation processes. Most of the alloying elements are present as intermetallic compounds in Mg-based alloys and beneficial to the mechanical properties. However, due to the very low corrosion potential of Mg, the second-phase particles typically acting as local cathodes cause internal galvanic corrosion, which accelerates the dissolution of Mg matrix [11–13]. Therefore, the application of Mg alloy implants has been restricted because of their high degradation rate and non-uniform degradation in the

physiological environment with pH of 7.40–7.60 and high chloride concentration [2,14,15]. Thus, it is of great importance to control the degradation rate of Mg alloys for biological applications.

Pure Mg with low concentrations of deleterious elements, i.e. Fe, Ni, Co and Cu, had been employed to improve corrosion resistance [16,17]. The high-purity Mg containing single phase microstructure performed stable and uniform in vitro and in vivo degradation and good bio-function as bone fixation implants [17]. In this work, we proposed to prepare new biodegradable single phase Mg alloys with some solutes in order to improve the corrosion resistance by avoiding the internal galvanic corrosion. Designing the single-phase Mg alloy, we should consider the solubility and biocompatibility of the alloying elements. According to the phase diagrams of Mg alloys, Al, Zn, Li and other limited number of elements have some solubility in the binary alloys; but only a few multivariate Mg alloys have single-phase microstructure, such as Mg–Al–Zn alloy [18]. And

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recently, Mg–Zn–Ag ternary phase diagram had been reported [19], which revealed that both Zn and Ag have a certain amount of solubility in Mg matrix. In Mg–Zn and Mg–Zn–Ag alloys, certain Zn and Ag as solute atoms can improve the corrosion resistance of the alloys, but due to the existence of the secondary phases, they still showed high corrosion rate [6,20,21]. On the other hand, Zn is one of the essential trace elements for human body. The Mg–Ag alloys had been studied as antibacterial biodegradable implants to solve the inflection problem during implant surgery [22]. Therefore, according to Mg–Zn–Ag ternary phase diagram, Mg–3Zn– x Ag ($x=0, 1, 3$, mass fraction, %) alloys were chosen to prepare single-phase Mg alloys by hot extrusion and solid solution treatment in present work. Immersion tests were applied to reveal the influence of the existence form of Zn and/or Ag on the corrosion resistance of Mg alloys, and the as-extruded pure Mg was selected as control. It is helpful to provide new ideas for biodegradable Mg alloys design through preparing single-phase Mg alloys in the future.

2 Experimental

Pure Mg, Mg–3Zn (ZQ30), Mg–3Zn–1Ag (ZQ31) and Mg–3Zn–3Ag (ZQ33) (mass fraction, %) alloys were prepared by melting magnesium (99.95%), zinc (99.995%) and silver (99.99%) ingots at 760 °C under the protection of N_2+SF_6 and then were cast into a steel mould kept at 300 °C. The homogenization treatment was carried out at 300 °C for 2 h and then 340 °C for 2 h. And then, the indirect extrusion was carried out at 300 °C with an extrusion ratio of 16:1, and cylindrical rod of 12 mm in diameter was obtained. Solution treatment of the as-extruded ZQ3 x alloys was carried out at 400 °C for 8 h, and then quenched into water.

The microstructure of Mg alloys was investigated by scanning electron microscopy (SEM, JEOL JSM–6510A) and X-ray diffractometry (XRD, X'pert Pro). Samples were cut perpendicular to the extrusion direction, and then ground with SiC paper up to 2000 grits, followed by mechanically polishing with 0.5 μ m diamond pastes. The XRD was carried out on the cross section with Cu target, voltage of 40 kV, current of 40 mA and scan rate of 3 (°)/min.

The immersion tests on the as-extruded and solid-solution treated Mg alloys were carried out in SBF with pH 7.40 in water bath to keep a constant temperature of 37 °C. The SBF solution contained 8.035 g/L NaCl, 0.355 g/L $NaHCO_3$, 0.225 g/L KCl, 0.231 g/L $K_2HPO_4 \cdot 3H_2O$, 0.311 g/L $MgCl_2 \cdot 6H_2O$, 39 mL/L HCl (1 mol/L), 0.292 g/L $CaCl_2$, 0.072 g/L Na_2SO_4 , 6.118 g/L TRIS and 0–5 mL/L HCl (1 mol/L). Prior to the degradation test, the samples were ground by

SiC paper up to 2000 grits, cleaned in ethanol, and then dried in warm flowing air. The corrosion products were removed by solution with 200 g/L CrO_3 , 10 g/L $AgNO_3$ and 20 g/L $Ba(NO_3)_2$. The mass loss of each sample was carefully recorded to calculate the degradation rate.

3 Results and discussion

The microstructure of the ZQ3 x alloys was characterized by the back-scattered electron (SEM–BSE) and XRD in Fig. 1 and Fig. 2, respectively. The as-extruded ZQ30 contained very fine second-phase particles (Fig. 1(a)). With Ag addition, there were second-phase particles with size between 0.3 and 6 μ m in the as-extruded ZQ31 and ZQ33 (in Figs. 1(b, c)). The XRD patterns confirmed that the secondary phase would be $Mg_{51}Zn_{20}$ and $Ag_{17}Mg_{54}$ (Fig. 2(a)), which agreed with the observation of the ZQ6 x alloys [20]. And as Ag content was increased from 0 to 3% (mass fraction), the intensity of the peaks of secondary phase increased, which agreed with the SEM–BSE observation in Figs. 1(a–c). Apart from the second phase particles, there was obvious atom segregation in the as-extruded alloys, which also meant the heterogeneous distribution of the alloying element. After the solution treatment, the segregation disappeared, and most of the secondary phases were dissolved in the Mg matrix, but a little amount of small secondary phase particles were still retained (as shown by the black arrows in Figs. 1(d–f)). It was also confirmed that very small amount of the secondary phases retained after the solution treatment by the XRD patterns in Fig. 2(b). Therefore, the quasi-single phase ZQ3 x alloys were obtained by solution treatment at 400 °C for 8 h.

The degradation rates of the as-extruded and solid-solution treated ZQ3 x alloys are shown in Fig. 3 according to the immersion tests. The degradation rate decreased with increasing the immersion time, and finally tended to a stable value when the immersion time was up to 4 days or more. It might be attributed to the fact that the corrosion products hindered the corrosion process to a certain extent. This revealed that the quasi-single phase ZQ3 x alloys had higher corrosion resistance than the corresponding multi-phase ZQ3 x alloys. The as-extruded pure Mg and ZQ30 tended to a same stable degradation rate. But the degradation rates significantly increased with Ag addition, which was also shown in the as-extruded ZQ6 x alloys [20]. Most of $Mg_{51}Zn_{20}$ and $Ag_{17}Mg_{54}$ particles dissolved after solution treatment. Both the solid-solution treated ZQ30 and ZQ31 alloys showed similar degradation rate to the as-extruded pure Mg and ZQ30 of about 20 g/($m^2 \cdot d$) (Figs. 3(a, b)). While the stable degradation rate of solid-solution treated ZQ33 was about 45 g/($m^2 \cdot d$) which

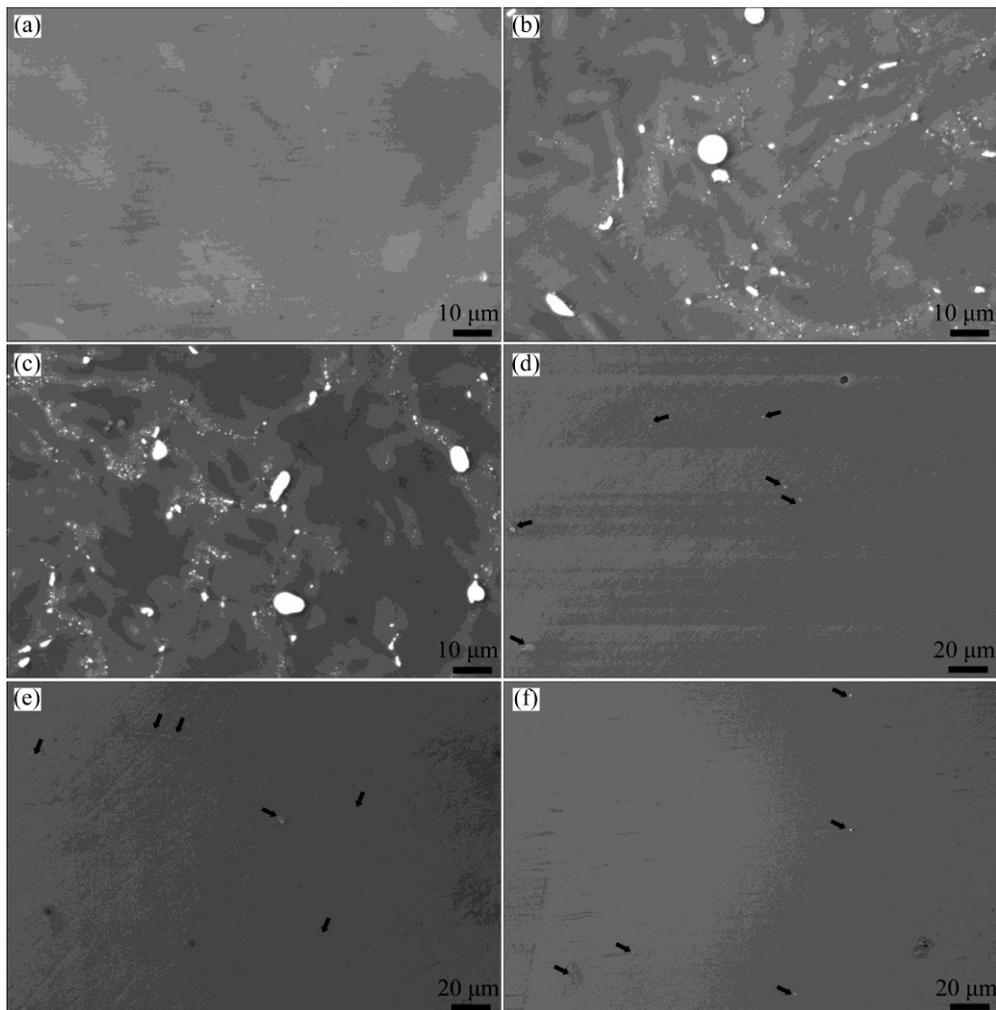


Fig. 1 Microstructures of as-extruded ZQ30 (a), ZQ31 (b), ZQ33 (c) and solid-solution treated ZQ30 (d), ZQ31 (e), ZQ33 (f) alloys (Black arrows show remaining second phase particles in solid-solution treated ZQ alloys)

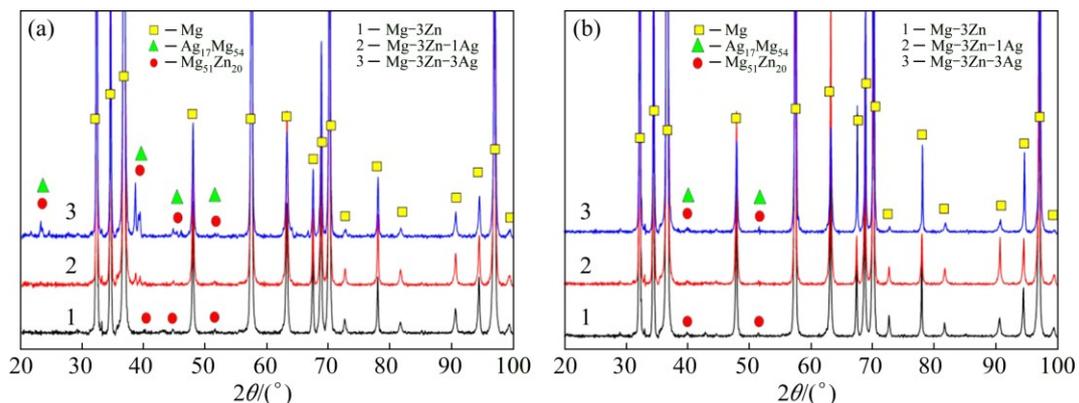


Fig. 2 XRD patterns of ZQ3x alloys: (a) As-extruded; (b) Solid-solution treated

was higher than that of pure Mg (Fig. 3(c)). This might be because the remaining secondary phases after solution treatment accelerated the degradation rates. So, there was no obvious change in the degradation rate of ZQ30 alloys after solution treatment, because some amounts of Zn existed as the atom segregation which had less negative

effect on corrosion resistance than second phase in the as-extruded ZQ30. On the other hand, the stable degradation rate of the solid-solution treated ZQ31 and ZQ33 was about half that of as-extruded alloys. So, the quasi-single phase ZQ31 and ZQ33 alloys had higher corrosion resistance than the corresponding as-extruded

alloys.

Figure 4 shows the macrographs of pure Mg and ZQ3x alloys after removing the products immersed in SBF for 8 days. The pure Mg showed flat surface, indicating the uniform degradation process (Fig. 4(a)). The as-extruded ZQ30 showed more serious localized corrosion than the solid-solution treated ZQ30 (Figs. 4(b, e)), though they showed similar degradation rate. The as-extruded ZQ31 and ZQ33 (Figs. 4(c, d)) exhibited obvious localized corrosion; especially, the ZQ33 had lost its shape integrity. The solid-solution treated ZQ31 and ZQ33 (Figs. 4(f, g)) kept the shape integrity, but the pitting corrosion still occurred on the surface more seriously with Ag addition. This might be caused by the remaining secondary phases. The localized corrosion holes on the surface of solid-solution treated ZQ3x alloys were smaller, shallower and more uniform than those on as-extruded ZQ3x alloys.

The effect of the second phases on the corrosion resistance of Mg alloys has been investigated for Mg–Zn-based alloys [23–25]. It can be concluded that if the second phases were only of a few hundred nanometers, no matter in a discrete or continuous

distribution, they would act as micro-cathodes to accelerate corrosion. In the present work, the as-extruded ZQ3x contained $Mg_{51}Zn_{20}$ and/or $Ag_{17}Mg_{54}$, and the amount of $Ag_{17}Mg_{54}$ increased with Ag addition. These second-phase particles would act as micro-cathodes causing internal galvanic corrosion to accelerate degradation. So, the degradation rate of as-extruded ZQ3x alloys increased with Ag addition and was higher than that of pure Mg. After solution treatment, most of $Mg_{51}Zn_{20}$ and $Ag_{17}Mg_{54}$ dissolved, and the solid-solution treated ZQ3x alloys showed obvious improvement in corrosion resistance. Besides, the solid-solution treated ZQ30 and ZQ31 showed similar degradation behavior to pure Mg. Therefore, it is feasible to slow down the degradation rate and reduce the tendency of severely localized corrosion by removing the secondary phase. Moreover, if the alloying elements exist as solute atoms in Mg matrix, it is possible to eliminate the potential negative impact on human body caused by the different size non-degradable second-phase particles. So, the quasi-single phase Mg alloys could be a candidate for designing bio-degradable Mg alloys with proper degradation rate for medical application.

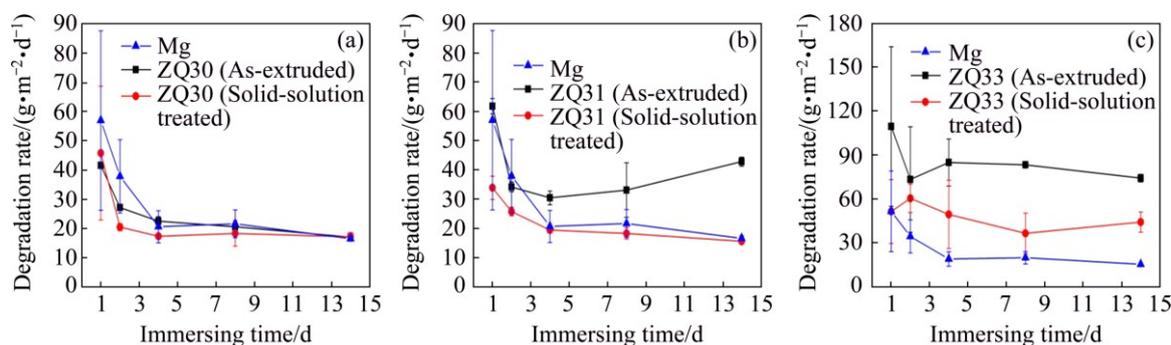


Fig. 3 Degradation rates of as-extruded and solid-solution treated ZQ30 (a), ZQ31 (b) and ZQ33 (c) alloys

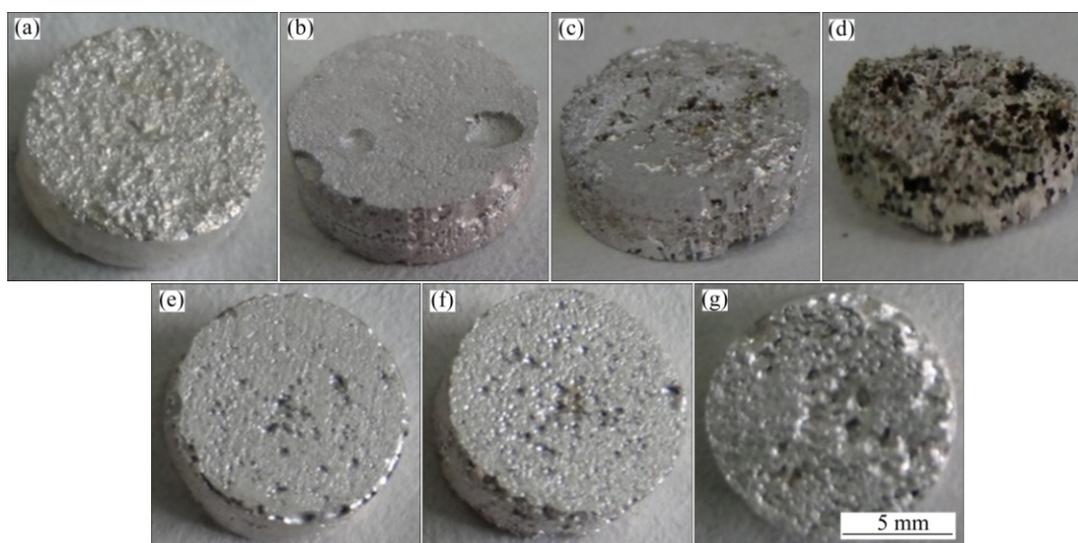


Fig. 4 Samples immersed in SBF for 8 d of as-extruded pure Mg (a), ZQ30 (b), ZQ31 (c), ZQ33 (d), and solid-solution treated ZQ30 (e), ZQ31 (f), ZQ33 (g) alloys

It is noted that the solution treatment at high temperature is unavoidable to lead to the grain growth of Mg matrix. But the grain refinement will improve the corrosion resistance (i.e., decrease the corrosion rate) according to the results of pure Mg and Mg–Zn alloys, which is attributed to easier passivation with high grain boundary density [26–28]. And also, it will improve the mechanical properties of Mg alloys according to Hall–Petch relationship. Therefore, in order to improve both the mechanical properties and corrosion resistance, the focus of the future work will try to refine the grains of the quasi-single phase Mg–Zn(–Ag) alloys by cold drawing and recrystallization annealing.

4 Conclusions

1) The as-extruded ZQ3x alloys contained Mg₅₁Zn₂₀ and Ag₁₇Mg₅₄ phases. And the quasi-single phase ZQ3x alloys were developed by solution treatment at 400 °C for 8 h.

2) The immersion tests indicated an improvement in the corrosion resistance and degradation uniformity of the quasi-single phase ZQ3x alloys due to the decrease of the amounts of Mg₅₁Zn₂₀ and Ag₁₇Mg₅₄ phases. And the degradation rate of quasi-single phase ZQ30 and ZQ31 alloys was equivalent to that of pure Mg. So, it could be an effective strategy for bio-degradable Mg alloys design to improve the corrosion resistance of magnesium itself by preparing the quasi-single phase Mg alloys.

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固溶处理对挤压态 Mg–Zn–Ag 合金体外降解速率的影响

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摘要: 对挤压态和固溶态 Mg–3Zn–xAg (x=0, 1, 3, 质量分数, %)合金在 37 °C 模拟人体体液中的降解行为进行对比研究, 并选择挤压态纯 Mg 作为参照。挤压态 Mg–Zn(–Ag)合金中存在 Mg₅₁Zn₂₀ 和 Ag₁₇Mg₅₄, 而经过 400 °C、8 h 固溶处理后获得了准单相的 Mg–Zn(–Ag) 合金。相比于挤压态合金, 准单相 Mg–Zn(–Ag)合金呈现出较低的降解速率和更加均匀的降解过程; 固溶态 Mg–3Zn–1Ag 和 Mg–3Zn–3Ag 合金的降解速率较挤压态的降低 50%, 接近挤压态纯 Mg 的降解速率。但与纯 Mg 相比, 准单相 Mg–Zn–Ag 合金表面仍发生一定程度的不均匀降解过程。所以, 通过制备单相 Mg 合金有望成为一种降低可降解生物 Mg 合金的降解速率的新方法。

关键词: 可降解 Mg 合金; Mg–Zn–Ag 合金; 固溶处理; 耐蚀性

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