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# 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 $Mg_{51}Zn_{20}$ and $Ag_{17}Mg_{54}$. 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 ZQ3x 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 μm 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 $NaHCO_3$, 0225 g/L KCl, 0.231 g/L $K_2HPO_4·3H_2O$, 0.311 g/L $MgCl_2·6H_2O$, 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 ZQ3x 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 μm 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 ZQ6x 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 ZQ3x alloys were obtained by solution treatment at 400 °C for 8 h.

The degradation rates of the as-extruded and solid-solution treated ZQ3x 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 ZQ3x alloys had higher corrosion resistance than the corresponding multi-phase ZQ3x 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 ZQ6x 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/($m^2$·d) (Figs. 3(a, b)). While the stable degradation rate of solid-solution treated ZQ33 was about 45 g/($m^2$·d) which