Microstructure, mechanical and corrosion properties of novel quaternary biodegradable extruded Mg-1Zn-0.2Ca-xAg alloys

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Abstract:

In the anastomotic surgery, the currently used degradable magnesium alloys are facing some bottleneck problems such as lower mechanical properties and slower degradation rate. In this study, the novel biodegradable extruded Mg–1Zn–0.2Ca–xAg (x=0, 1, 2, 4) alloys will be developed and the corresponding microstructure, mechanical, and corrosion properties after Ag addition will be investigated. The results indicate that with the Ag addition, the grain size is refined due to fully dynamic recrystallization and Ag_{17}Mg_{54} phase, an important strengthening phase, begin to be precipitated in the Ag-contained alloys. Due to the stronger solution strengthening and precipitation strengthening, the Mg–1Zn–0.2Ca–4Ag alloy attains the highest ultimate tensile strength among all the alloys. Moreover, Ag element also enhances the electrode potential of the matrix, reduces the susceptibility of pitting corrosion and accelerates the corrosion rate of the alloys by micro-galvanic corrosion between the second phases and the matrix from the analyses of corrosion products and 3D Volta potential map. As a result, 4Ag alloys attain the fastest degradation rate among all the alloys. Combing the mechanical and corrosion results, it can be seen that 4Ag alloys, as novel biodegradable magnesium alloys, can meet the requirement of anastomotic surgery preferably, exhibiting the better application prospects.

Key words: Mg alloy; extrusion; microstructure; mechanical and corrosion properties; anastomotic surgery.
1. Introduction

Magnesium alloys are capturing strong attention as potential implanted biomedical materials for medical applications due to the similar elastic modulus as that of human bone, their biodegradation in vivo without a second surgery for implant removal and the outstanding biocompatibility of the released magnesium ions[1-5]. It is advised that magnesium, an essential element of the human body, should be absorbed about 300–350mg every adult per day[6], which is beneficial for human metabolism. Furthermore, it is widely acknowledged that Mg$^{2+}$ ions can promote the bone tissue regeneration to shorten the fracture healing time[3, 5]. These attractive advantages provide magnesium alloy with application prospects in cardiovascular and orthopedic devices[7]. However, the further research is needed to expand access to the application of magnesium alloys by reason of low strength and uncontrollable corrosion rate[8].

There is a multitude of methods that can be used to strengthen the magnesium alloys. A quintessential example should be cited that an extrusion, the conventional thermomechanical processing, could reduce the microstructure defects, trigger dynamic recrystallization (DRX), and finally refine the grains. Another method is elemental alloying by adding Al, Zn, Ca, rare earth (RE) elements and so on[9-13]. Although the extruded RE-containing alloys exhibited better performance in the mechanical properties in particular, for instance, Mg-2.4Zn-0.8Gd alloy with a tensile yield strength (TYS) of 284 MPa and ultimate tensile strength (UTS) of 338 MPa[14], RE-free Mg alloys are more competitive for commercial utilization because of the biosafety [15]. According to our recent investigations[16-18], Mg-1.0Zn-0.2Ca alloy is promising as the base alloy for further alloy development if considering comprehensive mechanical and corrosion properties although its mechanical properties are still not enough for medical application.

On the other hand, compared with the wide application in the cardiovascular stent or orthopedics domains, that of anastomotic surgery was less concentrated relatively[19-22]. The wires or nails for anastomotic surgery demand the faster corrosion rate, i.e. entirely degradation in 1 or 2 weeks, different from the lower
corrosion rate in a bone nail or cardiovascular stent[3, 23]. As an example, Cai[24]
developed biodegradable Mg-2Zn wires for anastomotic surgery with an UTS up to
250MPa and ductility above 10%. However, as a candidate for anastomotic surgery
material, the major structure of Mg-2Zn still maintains relative integrity in vivo in 2
months which is far beyond the deadline of full biodegradation in the human body in 4
weeks[23]. Moreover, the strengths of the above two materials are not enough in animal
testing in vivo. For the requirement of anastomotic surgery materials[3, 23], it is
indispensable to design a novel degradable magnesium alloy with a faster degradation
rate and higher mechanical strength.

Ag is one key optional element for magnesium alloys since it is rewarding to strength improvement and corrosion rate regulation[25-28]. Tie et al claimed the Ag element improved the mechanical properties in the biodegradable alloy. With the content up to 6 wt.%, the UTS was doubled from pure magnesium(from 108.3 to 215.9MPa)[29]. It was lately revealed the addition of 8wt.% Ag in magnesium alloy accelerated the speed of the alloy degradation both in vitro and in vivo[30]. Moreover, the Ag element, which is noted for superior antibacterial property in the form of ion, is generally applied in the medical devices and products with its promising biosafety in the human body[31]. Nevertheless, the researchers pour more attention into binary or ternary Ag-contained magnesium alloy while little investigations have been focused on the multicomponent degradable extrusion magnesium alloy[25-30]. Considering the effect of the Ag element on strengthening mechanical properties and accelerating the corrosion rate, it is suitable to solve the above-mentioned problems faced by Mg-2Zn alloys as the anastomotic surgery materials.

In order to achieve the above aim, a series of novel quaternary Mg-1Zn-0.2Ca-
xAg alloy with different Ag contents were designed and prepared in this paper. The influence of Ag on the microstructure, mechanical, and corrosion properties of the extruded Mg–Zn–Ca-Ag alloys is studied particularly. Besides, the strengthening and corrosion mechanism of Ag elements in the Mg–Zn–Ca-Ag alloys is also explained.

2. Experimental procedures
The Mg-1Zn-0.2Ca-xAg alloys (x = 0, 1.0, 2.0, 4.0 wt.%, named as 0Ag, 1Ag, 2Ag, and 4Ag alloy hereafter) with the compositions illustrated in Table 1, were fabricated from high-purity Mg ingots, pure Zn particles, pure Ag particles and Mg-20Ca master alloy. The Mg ingots were heated by an electric resistance furnace and melt under the protection of a CO\(_2\) (99% vol.) and SF\(_6\) (1% vol.) mixed gas. Then pure Zn and pure Ag particles and Mg-Ca master alloy were mixed into the Mg melt at 700°C. After stirred by a graphite bar, the melt was held for 15min at 750°C for full elemental diffusion and then cast into a water-cooled steel mold at 700°C. The following heat treatment is at 450°C for 24 hours and quenched in water before extrusion. Then the ingots were extruded into the rods from 85mm to 16 mm in diameter, i.e. an extruded ratio of about 28, at 350°C.

In order to characterize the microstructure of the alloys, the scanning electron microscope (SEM, Phenom XL) equipped with energy disperse spectroscopy (EDS) and the electron backscatter diffraction (EBSD, Supra 55) and the optical microscope (OM, Carl ZEISS Axio Imager A2M) were applied. The specimens which are cut along the extruded direction (ED) were grounded and polished for SEM observation, and then etched by 5.5g picric acid + 2ml acetic acid + 90ml absolute ethanol + 10ml distilled water for OM observation[32]. The samples for EBSD observation were electro-polished at −20°C cooled by liquid nitrogen with a 20 V applied potential and a 0.2 A current. The phase analysis of the extruded Mg-Zn-Ca-Ag alloys was performed by an X-ray diffractometer (XRD, Rigaku DMAX-RB). The transmission electron microscope (TEM, Tecnai G2 F20) was utilized for the further phase analysis, whose samples were prepared with ion thinning.

The extruded rods were cut into dog bone tensile test specimens (3 specimens with a gauge of 25 mm in length for each alloy) along the extrusion direction and a material testing machine (Instron5569) was used in this study. The simulated body fluid (SBF) solution according to the procedure in Ref.[33] was used for the immersion test in vitro at 37 ± 0.5°C. After 7 days, the samples were taken out and immersed in the 200g/L CrO\(_3\) + 10g/L AgNO\(_3\) solution to eliminate corrosion products to observe the
morphology by SEM [34]. Scanning Kelvin probe force microscopy (SKPFM, Dimension FastScan) was introduced to characterize the relative potential of the second phase and the $\alpha$-Mg matrix for further analyzing the corrosion mechanism.

3. Results

3.1. As-extruded microstructure

As presented in Fig.1, from the optical micrographs (OM) of the Mg-1.0Zn-0.2Ca-xAg alloys obvious grain refinement can be observed due to the Ag addition. The average size of the DRX grains is 9.8$\mu$m, 7.35$\mu$m, 6.45$\mu$m, 5.36$\mu$m respectively, with the Ag addition from 0 to 4 wt.%. The SEM results are also demonstrated in Fig.2, indicating the more phases precipitation with increasing Ag content. There are quite a few second phases precipitated in the Mg matrix under 2wt.% Ag content, whereas massive tiny particular second phases less than 0.5$\mu$m appear in the 4Ag alloy, which gives rise to favorable precipitation strengthening and grain refinement.

The further phase analysis of the alloy is characterized by XRD and the patterns are depicted in Fig.3. A strong intensity of Mg matrix peaks is observed in this sample. In contrast, quite weak diffraction peaks of the second phase are displayed owing to the low alloying content and the low volume fraction of the second phase, especially in 1Ag and 2Ag alloy. Thus, from the XRD results, $\alpha$-Mg + Ca$_2$Mg$_6$Zn$_3$ are observed for 0Ag and $\alpha$-Mg + Ag$_{17}$Mg$_{54}$ peaks are observed for 4Ag alloys, respectively. Since it is arduous to characterize all certain second phases only by the XRD patterns, TEM can be introduced for the further analysis of the second phases in the investigated alloys.

Fig.4 represents the TEM results and the corresponding selected area diffraction patterns (SADPs) for the extrusion Mg-1.0Zn-0.2Ca-xAg alloys. The precipitated phase with the triangular granule shown in Fig.4a is Ca$_2$Mg$_6$Zn$_3$, identified by the SADPs in Fig.4e, taken along [2-1-10] zone axis. The second phase contains 76.2 at% Mg, 12.4 at% Zn and 11.4 at% Ca by EDS shown in Fig.4(g), which confirms the 0Ag alloy consists of $\alpha$-Mg and Ca$_2$Mg$_6$Zn$_3$. Observed from Fig.4b, the second phase with an elliptical shape and approximate 0.25$\mu$m size can be speculated to be the binary Ag$_{17}$Mg$_{54}$ phase for the 1Ag alloy from the corresponding SADPs manifested in Fig.4f. The second phase in the 2Ag alloy, shown in Fig.4c, keep roughly as same as that of
1Ag alloy no matter the morphology or the component. Thus, it can be inferred that both 1Ag and 2Ag alloy mainly consist of $\alpha$-Mg matrix and the binary $\text{Ag}_{17}\text{Mg}_{54}$ phases. The TEM images of the 4Ag alloy are exhibited in Fig.4d. There are quite a few circular phases are observed from the SEM results in Fig.3. One of those circular phases is identified as $\text{Ag}_{17}\text{Mg}_{54}$ with the EDS results containing 85.5at%Mg and 14.5at%Ag as seen in Fig.4(h). This indicates the main strengthening second phase is $\text{Ag}_{17}\text{Mg}_{54}$ in 4Ag alloy. Also, the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase is not observed in Ag-contained alloys and the reason will be discussed the later.

EBSD is applied to investigate texture evolution under the influence of the Ag element. EBSD orientation map, (0002) pole figure (PF) and inverse pole figure (IPF) of all the Mg-Zn-Ca-xAg alloy are presented in Fig. 5, respectively. The extruded alloy exhibits a fully DRX and comparatively uniform microstructure, nevertheless the grain size and texture intensity are not the same. Fig. 5a exhibits the (0002) pole figures of the 0Ag alloy. The basal poles of the extruded Mg-Zn-Ca-Ag alloys are parallel to the extrusion direction, which is generally regard as a typical texture of Mg alloys after extrusion. The extruded texture and basal poles are alike in the alloys with a relatively low angle distribution away from the transverse direction (TD), as seen in Fig.5 (b-d). The 0Ag alloy exhibit the strongest intensity (5.67) and the concentrated textures intensity distribution. With the addition of Ag, the modification with basal planes expand within a wider range from ND and the textures intensity slump to 3.00. The textures intensity keeps no significant change at a range of about 3.0~3.2 with a further addition of Ag element. From the IPFs of the alloys seen in Fig.5, the 0Ag alloy presents a fiber texture with $[10\bar{1}0]$ orientation parallel to the extrusion direction. Then the fiber textures extend from $[10\bar{1}0]$ to $[2\bar{1}0\bar{1}]$ orientation with the more Ag addition. Meanwhile, the intensity of the fiber texture drops to 1.73 in 4Ag alloy.

### 3.2. Mechanical and corrosion properties

The tensile strength is a vital property as the biodegradable alloy. The mechanical properties of Mg–1Zn–0.2Ca-xAg alloys at room temperature and the corresponding stress-strain curves are shown in Fig.6. The TYS and UTS increase almost
monotonically with Ag addition from 0 wt.% to 4 wt.%. Compared to 0Ag alloy, the increased amplitude is very significant in all cases. Especially, for the 4Ag alloys, TYS and UTS can reach 153MPa and 267MPa, respectively, which is far larger than 0Ag alloys. The 4Ag alloy almost doubtless precede to the other alloys in regards to the mechanical properties. What is more interesting, all the alloys hold a high level of elongation. Although the variation trend of alloy plasticity keeps reduced on the whole, the lowest elongation is still over 25%. The 0Ag alloy has excellent plasticity with the highest elongation (31%). For further thermomechanical processing such as hot or cold drawing, these magnesium alloys with decent plasticity will obtain much processing window [35].

The corrosion control of different Mg–1Zn–0.2Ca–xAg alloys are also compared in this paper. Fig.7a exhibits the macrographs after immersed in SBF solution for 7 days. For 0Ag, 1Ag and 2Ag alloys, the samples with a layer of corrosion products on the surface are still integrated. There are some deeper corrosion pits around the white surface for 0Ag alloy. For the 1Ag alloy, a relatively smooth surface with yellow products can be observed while 2Ag alloy can exhibit one corrosion channel on the surface. Serious corrosion behavior occurred in the 4Ag alloy with some matrix exfoliation around the corner and a multitude of white dots on the surface were observed. The samples were also weighed after the corrosion products cleaned in order to evaluate the corrosion property of each alloy quantitatively. Fig. 7(b) illustrates that the corrosion curve first decrease with Ag content from 0wt.% to 1wt.% Then the corrosion rate increase with Ag content over 1wt.%, and jump exceedingly fast to 4.29 mg/cm²/day with the addition of 4wt.% Ag especially. The minimum corrosion rate corresponds to 1Ag alloy, which is in accordance with corrosion morphologies mentioned above.

Fig.8 exhibits the surface morphologies of different Ag-contained samples before removing corrosion products. It can be observed that the insoluble corrosion products with a lot of cracks was exposed on the surface of different alloys shown in Fig.8, which is ascribed to the dehydration of the surface layer in the air. For the 1Ag alloy, the smallest crack among the alloys can be observed. The thickness between 0Ag and 2Ag
alloy is nearly the same. A few white products begin to appear when Ag content is over 2wt.%. It is apparently shown that the crack in the corrosion surface of 4Ag alloy are the widest and deepest. The roughest skin with a lot of white trick particles is confirmed to be Ag-rich corrosion products from EDS results shown in Fig.8 (c)(d).

Fig.9 displays the surface morphologies of different Ag-contained samples after removing corrosion products. It is seen that there exists a mass of pitting corrosion zones and even some deeper holes observed in some areas of 0Ag alloy. The surface of 1Ag alloy is flat with seldom corrosion holes around and 2Ag alloy possesses more corrosion holes. Compared with these alloys, the surface is damaged more dramatically with lots of corrosion holes and grooves distribute all around the sample which is indicative of serious corrosion behavior formed for 4Ag alloy. The surface morphologies of the Ag-contained samples are fully following the corrosion rate curve shown in Fig.7b.

4. Discussion

The XRD and TEM images indicate that 0Ag alloy composes by $\alpha$-Mg + Ca$_2$Mg$_6$Zn$_3$ phase. For the 1Ag and 2Ag alloy, $\alpha$-Mg and a small amount of Ag$_{17}$Mg$_{54}$ phase can be observed while 4Ag alloy consists of $\alpha$-Mg and a large amount of Ag$_{17}$Mg$_{54}$ phase. The lack of Ca$_2$Mg$_6$Zn$_3$ phase in Ag-contain alloys may result from the silver element dissolved in the Mg-matrix which change the axial ratio of $\alpha$-Mg and promote the resolution of Zn and Ca element. An investigation also described that the mixing enthalpy of Mg–Zn ($-4$ kJ/mol) and Mg–Ca ($-6$ kJ/mol) is less than that of Mg–Ag ($-10$ kJ/mol.))$^{[36]}$, thus manifesting that the Mg atoms bond more easily with the Ag than the Zn and Ca atoms. Son et al.$^{[37]}$ concludes that the addition of Ag in Mg–6Zn–0.4Mn-based alloy can lead to the precipitation of the Ag$_{17}$Mg$_{54}$ phase, which was also found in Liu’s study$^{[30]}$. In this paper, Ag$_{17}$Mg$_{54}$ phase ($a=14.240\,\text{Å}, b=14.209\,\text{Å}, c=14.663\,\text{Å}, \alpha=\beta=\gamma=90^\circ$) is also the main strengthening second phase in the Ag-containing alloys after analyzing the XRD and TEM results shown in Fig.3 and Fig.4. From the previous studies, it was reported that the increase of the TYS is attributed to the second phase strengthening in as-cast alloy$^{[38]}$. For the 1Ag and 2Ag alloy, we naturally focus on the solution strengthening since the alloy precipitations are less
beyond the solution limits of each element shown from Fig.2. With the addition of Ag element is up to 4wt.%, the Ag_{17}Mg_{54} phase begins to be precipitated obviously, which has a strong effect to nailing the dislocation, and grain refinement, leading to an improvement of mechanical properties[29, 37]. As a result, the 4Ag alloy attains the maximum values of UTS and TYS, which is higher than the Mg-2Zn as the biodegradable anastomotic materials[24]. Meanwhile, all the Ag-contains alloys maintain excellent plasticity with the elongation of above 25% among these alloys.

The texture of the alloys distributes relatively randomly with the increase of Ag contents. From Fig.5, the additions of Ag element to Mg–Zn–Ca ternary alloy have a significant effect on the extrusion texture, which weakens the overall texture. In summary, two main mechanisms is widely introduced to explain texture change in magnesium alloys, i.e. the solid solubility of the alloying element, and the particle-stimulated nucleation(PSN) of recrystallization [39-41]. When the Ag content increases from 0 to 1wt.%, the silver element dissolved in the Mg-matrix will change both the stacking fault energy and axial ratio (c/a)[25, 40, 41], which are intensely vital physical properties of magnesium alloy, accordingly influencing the dislocation slip and DRX in the process of extrusion. However, when the Ag content increases up to 4wt.%, which is far beyond the maximum solubility of Ag in Mg at room temperature [42], it can be inferred that the weakened texture in the extruded alloys is not mainly caused by the solid solubility of the Ag element. As is reported recently, there also exists the effect of texture intensity reduction when adding Ca[40] or Sr[43] element in the magnesium alloy, and both are attributed to the second factor, i.e. PSN. After hot extrusion, both the matrix and the second phase are refined, distributed in the DRX grains or on their boundaries, which can hinder the growth of DRX grains[39-41, 43]. Therefore, the foregoing reports reveal that with the increase of Ag contents, many second phases induce the larger and wider recrystallization nucleation, which help to weaken the overall texture with random orientations. In a word, it can be inferred that PSN is the main reason for the modification of texture with Ag addition. Besides, as demonstrated in Fig.5, the volume fraction of DRX grains is extremely high with little twinning which mainly ascribes to high Ag contents and high extrusion temperature (350℃)[35]. The
relatively high Ag contents of 4wt.% spark off the formation of a sea of $\text{Ag}_{17}\text{Mg}_{54}$ second phases in the magnesium alloy, where the DRX process is adequately developed. A high extrusion temperature (350°C) is also reasonable since it can perform the DRX process in the twinned areas[35]. It is deemed that the magnesium alloys with refined microstructures and pleasurable grain orientations are expected to have more favorable formability for post-extrusion applications[35, 44].

The mechanical properties, especially for the TYS, are not only prominently influenced by the grain size according to the Hall-Petch formula but also by the textures [44]. As demonstrated in Fig.6, the TYS of 1Ag and 2Ag alloy climb so slowly which may result from the texture weakening. In this study, Ag also plays a more crucial role in grain refinement. Though considering the texture weakening, the precipitation strengthening and solution strengthening have a more powerful influence on the mechanical properties in the Ag-containing alloys. Up to 4wt.% Ag, the alloys achieve the most excellent comprehensive mechanical performance because of the second phase precipitation strengthening and grain refinement.

From Fig. 7(b), it exhibits that the corrosion rate first declines and then increases when Ag element is added from 0wt% to 4wt%. The minimum value is attained for the 1.0Ag alloy, which reveals this alloy shows the most excellent corrosion resistance among the investigated alloys. The standard electrode potential of the Ag element is +0.7996V while Mg is -2.375V[45]. Therefore, it can be inferred that one of the reasons why 1Ag alloy has a lower corrosion rate is that Ag, as a solution element in the $\alpha$-Mg matrix, enhances the standard electrode potential of the alloys[3, 18]. For further analysis of the corrosion mechanism, the 3-D Volta potential map and the corresponding line data of 0Ag, 1Ag, and 4Ag from SKPFM are performed in Fig.10, respectively. The mean potentials of the matrix are about 25mV, 35mV and 43mV, respectively, for 0Ag, 1Ag and 4Ag specimens, which apparently rises linearly. The Volta potential of the second phase is about -30~50mV, which is obviously lower than that of the matrix.

As illustrated in Fig.10, the corrosion potential of the $\text{Ag}_{17}\text{Mg}_{54}$ phase moves to a positive electrode due to the Ag addition[30, 46]. Therefore, the surface micro-galvanic corrosion is shifted to a circumstance which could lead to faster homogeneous corrosion
and minimize pitting corrosion[29, 46]. Pitting corrosion was controlled by this effect, which can explain why the 1Ag and 2Ag alloy can exhibit a less pitting corrosion susceptibility than 0Ag alloy displayed in Fig.8. It can be inferred that a bit addition of Ag could improve the corrosion forms and the controllable homogeneous corrosion is always better than partial pitting corrosion. Although the mean matrix potential of 4Ag alloy is the highest, the more second phases distributed in the alloys form numerous micro-galvanic corrosion cells on the surface. It rapidly accelerates the corrosion rate of the whole extruded alloy sample. Hence, 4Ag alloy exhibits the most severe electrochemical corrosion reaction because of the existence of a host of second phases precipitated. In a word, the addition of Ag can be a promising method to control both the corrosion forms and the corrosion rate.

On the other hand, compared with the Mg-Zn alloy as biodegradable anastomotic materials, biosafety should be considered with the relatively high content of Ag, especially with a high degradation rate. The total weight of Mg-Zn-Ca-Ag alloy nails for anastomotic surgery implanted in vivo is about 30-40 mg so that the degradation amount per day of the Ag element is much small. Besides, the preliminary tests of 4Ag alloy are performed by Li’s research[23] and it confirmed that the alloy appeared to be both responsible for bio-safety and excellent biocompatibility. The corresponding paper will be published elsewhere. Consequently, combing the mechanical and corrosion results, it can be seen that 4Ag alloys, as a novel biodegradable magnesium alloy, can meet the requirement of anastomotic surgery preferably, exhibiting the potential better application prospects.

5. Conclusion

With the addition of the Ag element, the grain size is refined in the Mg–1.0Zn–0.2Ca-xAg alloys due to fully dynamic recrystallization. The Ag element significantly influences the quantity of the second phase, the textures, the mechanical properties, and the corrosion properties in the Mg–1.0Zn–0.2Ca-xAg alloys. The following conclusions were derived:

(1) The Ag addition generate the formation of a binary Ag$_{17}$Mg$_{54}$ phase. Besides, the precipitation amounts of the Ag$_{17}$Mg$_{54}$ increase with high Ag content.
(2) The 4Ag alloy attains the highest UTS (267 MPa) and YS (153 MPa) due to the more refined grains and the strengthening effect of the second phase. The Mg–1.0Zn–0.2Ca-xAg alloys all keep excellent elongation of over 25%.

(3) The addition of Ag has a huge effect on weakening the overall textures, which is attributed to the PSN of recrystallization, thereby influencing the mechanical properties.

(4) With the increase of Ag contents from 0wt.% to 1wt.%, the corrosion curve first decrease. Then the corrosion rate increase with Ag content over 1wt.% A minimum corrosion rate can be attained for the 1Ag alloy and a maximum one for the 4Ag alloy, which can be speculated from the dissolution of Ag element and difference of the quantity diverse precipitated phases which stimulate the electrochemical corrosion reaction.

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0.5Ca alloy. MATER LETT 2009;63:557.


Tables and Figure Captions

Table 1 The composition of the Mg-1.0Zn-0.2Ca-xAg alloys.

Fig.1 The microstructure of extruded Mg–1Zn–0.2Ca-xAg alloys observed by OM perpendicular to the extruded direction: (a) 0Ag; (b) 1Ag; (c) 2Ag; (d) 4Ag.

Fig.2 The microstructure of extruded Mg–1Zn–0.2Ca-xAg alloys observed by SEM perpendicular to the extruded direction: (a) 0Ag; (b) 1Ag; (c) 2Ag; (d) 4Ag.

Fig.3 XRD patterns of the extruded Mg–1Zn–0.2Ca-xAg specimens.

Fig.4 TEM bright-field images of the extruded alloy and the corresponding SADPs: (a) TEM bright-field images of 0Ag alloy; (b) TEM bright-field images of 1Ag alloy; (c) TEM bright-field images of 2Ag alloy; (d) TEM bright-field images of 4Ag alloy; (e) SADP for Ca$_2$Mg$_6$Zn$_3$ shown in (a); (f) SADP for Ag$_{17}$Mg$_{54}$ phase shown in (b-d); (g) EDS analysis for Ca$_2$Mg$_6$Zn$_3$ phase shown in (a); (h) EDS analysis for Ag$_{17}$Mg$_{54}$ phase shown in (b-d).

Fig.5 EBSD orientation map, the corresponding (0002) pole figure and inverse pole figure of (a)0Ag alloy (b)1Ag alloy (c)2Ag alloy (d) 4Ag alloy.

Fig.6 Mechanical properties (a) and stress–strain curves (b) of the extruded Mg–1Zn–0.2Ca-xAg alloys.

Fig.7 The surface macrograph without removing the surface corrosion products (a) and the curve of the corrosion rate (b) of Mg–1Zn–0.2Ca-xAg alloys after being immersed in SBF solution for 168 h at 37°C.

Fig.8 SEM micrographs of the surface morphology of samples with corrosion products for Mg–1Zn–0.2Ca-xAg alloys: (a) 0Ag; (b) 1Ag; (c) 2Ag; (d) 4Ag.

Fig.9 SEM micrographs of the surface morphology of samples without corrosion products for Mg–1Zn–0.2Ca-xAg alloys: (a) 0Ag; (b) 1Ag; (c) 2Ag; (d) 4Ag.

Fig.10 The 3-D Volta potential map and the corresponding line data of 0Ag(a), 1Ag(b) and 4Ag(c) from SKPFM.
Table 1

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<th>Zn (wt.%)</th>
<th>Ca (wt.%)</th>
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Fig. 1.
Fig. 2
Fig. 3

![X-ray diffraction patterns for different samples](image)
Fig. 5

(a)  

Max=5.67

(b)  

Max=3.17

Max=2.77
(c) 

(0002) ND

Max=3.00

(d) 

(0002) ND

Max=3.19
Fig. 6

(a) Tensile properties of the Ag-infiltrated PVA films as a function of Ag content. The symbols represent the experimental data, while the bars indicate the standard deviation. The solid lines are fits to the data. The UTS and TYS values are indicated above the bars. The elongation values are shown on the right axis.

(b) Stress-strain curves for the Ag-infiltrated PVA films. The curves are labeled with the Ag content (0Ag, 1Ag, 2Ag, 4Ag). The stress is shown on the left axis, and the strain is shown on the right axis.
Fig. 7

(a)

(b)

![Corrosion image and graph showing Ag content vs. corrosion rate in SBF.](image-url)
Fig. 8

(a)  

(b)  

(c)  

(d)  

Ag-rich products

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Fig. 9

(a) Fatigue Zone

(b) Holes

(c) Corrosion Groove

(d) 100μm

100μm
Fig. 10

(a) 

(b) 

(c)