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 Ag₁₋₁Mgₓ₄ 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. Combining 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.

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 ∼ 350 mg every adult per day [6], which is beneficial for human metabolism. Furthermore, it is widely acknowledged that Mg²⁺ 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 215.9 MPa) [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 CO2 (99% vol.) and SF6 (1% vol.) mixed gas. Then pure Zn and pure Ag particles and Mg-2Ca master alloy were mixed into the Mg melt at 700 °C. After stirred by a graphite bar, the melt was held for 15 min 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 h and quenched in water before extrusion. Then the ingots were extruded into the rods from 85 mm 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 +2 ml acetic acid +90 ml absolute ethanol +10 ml 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.

| Alloy | Mg(wt%) | Zn(wt%) | Ca(wt%) | Ag(wt%) |
|-------|---------|---------|---------|---------|
| 0Ag   | Bal.    | 1.00    | 0.20    | 0.00    |
| 1Ag   | Bal.    | 1.00    | 0.20    | 0.84    |
| 2Ag   | Bal.    | 1.00    | 0.20    | 1.60    |
| 4Ag   | Bal.    | 1.00    | 0.20    | 3.54    |

Table 1. The composition of the Mg-1.0Zn-0.2Ca-xAg alloys.
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 (Instron 5569) was used in this study. The simulated body fluid (SBF) solution according to the procedure in [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 200 g l \(^{-1}\) CrO\(_3\) + 10 g l \(^{-1}\) 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 figure 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 μm, 7.35 μm, 6.45 μm, 5.36 μm respectively, with the Ag addition from 0 to 4 wt%. The SEM results are also demonstrated in figure 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 μm 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 figure 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.

Figure 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 figure 4(a) is Ca\(_2\)Mg\(_6\)Zn\(_3\), identified by the SADPs in figure 4(e), 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 figure 4(g), which confirms the 0Ag alloy consists of \(\alpha\)-Mg and Ca\(_2\)Mg\(_6\)Zn\(_3\). Observed from figure 4(b), the second phase with an elliptical shape and approximate

![Figure 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.](image-url)
0.25 μm size can be speculated to be the binary Ag17Mg54 phase for the 1Ag alloy from the corresponding SADPs manifested in figure 4(f). The second phase in the 2Ag alloy, shown in figure 4(c), 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 α-Mg matrix and the binary Ag17Mg54 phases. The TEM images of the 4Ag alloy are exhibited in figure 4(d). There are quite a few circular phases are observed from the SEM results in figure 3. One of those circular phases is identified as Ag17Mg54 with the EDS results containing 85.5at%Mg and 14.5at% Ag as seen in

Figure 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.

Figure 3. XRD patterns of the extruded Mg–1Zn–0.2Ca–xAg specimens.
Figure 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).

This indicates the main strengthening second phase is Ag$_{17}$Mg$_{54}$ in 4Ag alloy. Also, the Ca$_2$Mg$_6$Zn$_3$ phase is not observed in Ag-contained alloys and the reason will be discussed 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 figure 5, respectively. The extruded alloy exhibits a fully DRX and comparatively uniform microstructure, nevertheless the grain size and texture intensity are not the same. Figure 5(a) 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 regarded 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 figures 5(b)–(d). The 0Ag alloy exhibits 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 figure 5, the 0Ag alloy presents a fiber texture with [10–10] orientation parallel to the extrusion direction. Then the fiber textures extend from [10–10] to [2–1–10] 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 figure 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 153 MPa and 267 MPa, respectively, which is far larger than 0Ag alloys. The 4Ag alloy almost doubtlessly 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. Figure 7(a) 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. Figure 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 cm$^{-2}$/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.

Figure 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 figure 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 figures 8(c), (d).

Figure 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 figure 7(b).
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$^{-1}$) and Mg–Ca ($-6$ kJ mol$^{-1}$) is less than that of Mg–Ag ($-10$ kJ mol$^{-1}$) [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–2Sn–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 ($a = 14.240$ Å, $b = 14.209$ Å, $c = 14.663$ 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 figures 3 and 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 figure 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 figure 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 4 wt%, 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 figure 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 °C) [35]. The relatively high Ag contents of 4wt% spark off the formation of a sea of Ag17Mg54 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 figure 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 figure 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 +0.7996 V while Mg is −2.375 V [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 α-Mg matrix, enhances the standard electrode potential of the alloys [3, 18].

Figure 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.

From figure 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 +0.7996 V while Mg is −2.375 V [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 α-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 figure 10, respectively. The mean potentials of the matrix are about 25 mV, 35 mV and 43 mV, respectively, for 0Ag, 1Ag and 4Ag specimens, which apparently rises linearly. The Volta potential of the second phase is about −30 ~ −50 mV, which is obviously lower than that of the matrix. As illustrated in figure 10, the corrosion potential of the Ag17Mg54 phase moves to a positive electrode due to the Ag addition [30, 46]. Therefore, the surface microgalvanic 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 figure 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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