



In-vitro corrosion and mechanical degradation of Mg-2Zn-0.2Ca-xAg alloys in Hanks' solution

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ABSTRACT

Mg-Zn-Ca-Ag alloys are considered promising biodegradable materials due to their excellent mechanical properties and biocompatibility; however, their corrosion behavior under physiological conditions is not yet fully understood for biomedical applications. In this study, the effects of Ag content on the microstructure and *in-vitro* corrosion behavior of Mg-2Zn-0.3Ca-xAg ($x = 0, 0.1, 0.3, 0.5$ wt%) alloys in Hanks' solution were systematically investigated. The results showed that Ag addition promoted dynamic recrystallization and refined the secondary phases without changing the overall phase composition, although moderate grain coarsening was observed. The alloy containing 0.1 wt% Ag exhibited the lowest degradation rate (0.10 ± 0.03 mm/year), while higher Ag contents accelerated corrosion. Moreover, Ag promoted the deposition of calcium phosphate compounds on top of corrosion products composed mainly of $\text{Mg}(\text{OH})_2$. The mechanical performance of the samples degrades with immersion, but are still sufficiently better than that of the natural bone. These findings suggest that controlled Ag addition can optimize both the degradation behavior, mechanical performance and surface bioactivity of Mg-Zn-Ca-based alloys, with minor addition of 0.1 wt% Ag offering the most favorable balance for biomedical applications.

1. Introduction

Magnesium alloys are promising biodegradable implants due to their close elastic modulus to the natural bone, favorable biocompatibility, and natural degradability, which can eliminate the need for secondary removal surgery [1,2]. Magnesium ions released during degradation participate in metabolic processes and facilitate bone and tissue regeneration [3]. However, their excessively high degradation rate can compromise mechanical integrity before complete tissue healing and cause local alkalization and hydrogen accumulation. Controlling the corrosion behavior of Mg alloys while maintaining sufficient mechanical and biological performance remains a critical challenge for clinical application.

Alloying magnesium with appropriate elements is the most effective approach to simultaneously optimize its mechanical strength,

biocompatibility, and degradation rate [4]. Zinc and calcium, as essential components of natural bone, are frequently incorporated into Mg to enhance its bioactivity. The mechanical strength of Mg can be enhanced by Zn through solid-solution strengthening and the precipitation of binary Mg-Zn phases (like Mg_7Zn_3 and MgZn) [5]. This strengthening effect is further improved when Ca is added to the Mg-Zn alloy, as it promotes the formation of additional ternary Mg-Zn-Ca precipitates [6]. The corrosion rate of the Mg-Zn-Ca alloys depends strongly on the contents of Zn and Ca [7,8]. Higher Zn and Ca contents increased the secondary phases density to strengthen the alloy, however, the degradation behavior may be compromised due to the enhanced galvanic corrosion. To mitigate this adverse effect, it has been suggested that Zn content should not exceed 4 wt% [9]. Moreover, excessive Ca addition can lead to alloy cracking during casting and a reduction in extrusion speed, a minor addition of less than 1 wt% Ca is normally

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suggested sufficient to enhance the bioactivity of Mg alloys [10]. Therefore, considerable research has focused on biodegradable Mg alloys with dilute Zn and Ca additions [11], among which Mg-2Zn-0.2Ca has shown particularly promising results [12].

Although Mg-Zn-Ca alloys have already been successfully commercialized for biomedical implants, ongoing research continues to focus on enhancing their antibacterial properties. Various strategies have been explored, including bulk drug incorporation [13], surface modification [14,15], and the addition of alloying elements with intrinsic antibacterial activity [16,17]. Among these, alloying with Ag is regarded one of the most effective, as Ag effectively inhibits the proliferation of a broad spectrum of bacteria [18]. Moreover, Ag is commonly used in Mg alloys, where it contributes to microstructural refinement and helps regulate the degradation rate [19]. Previous studies have demonstrated that incorporating an appropriate amount of Ag into Mg alloys can simultaneously improve mechanical properties, slow down biodegradation, and inhibit bacterial proliferation [20]. Nevertheless, determining the “appropriate” Ag content remains a considerable challenge [19,21–24], as it depends strongly on the dominant alloying elements and their concentrations. To date, the optimal Ag concentration in Mg-Zn-Ca-xAg alloys has yet to be established.

Moreover, Load-bearing implants are required to maintain their mechanical integrity throughout the tissue's healing process. This presents a specific challenge for biodegradable magnesium implants, as their mechanical properties inevitably decline due to corrosion. Consequently, a key concern is whether their residual strength remains adequate during this critical period. However, the mechanical degradation of Mg-Zn-Ca alloys, particularly with the addition of Ag, is not yet fully understood.

Therefore, the present study investigated the effects of Ag addition on the microstructural characteristics, biodegradation behavior and mechanical performance of the Mg-2Zn-0.2Ca alloy, with the aim of developing a novel biodegradable Mg alloy for bone fixation applications.

2. Materials and methods

2.1. Sample preparation

The Mg-2Zn-0.2Ca-xAg alloys used in this study were prepared through melting and subsequent casting. High-purity Mg ingots, zinc granules, Mg-25 wt% Ca master alloy, and Ag billets were melted under an argon (Ar) protective atmosphere. Once all the raw materials were completely melted, the molten alloy was subjected to direct-chill casting to produce ingots with a diameter of 140 mm. The as-cast ingots were then homogenized at 385°C for 20 h. Thereafter, the ingots were extruded at a ram speed of 0.6 mm/s with an extrusion ratio of 11:1, resulting in extruded rods with a diameter of 38 mm. The alloys with different Ag contents were designated as ZX20, ZXQ0.1, ZXQ0.3, and ZXQ0.5, corresponding to Ag contents of 0, 0.1, 0.3, and 0.5 wt%, respectively. The actual compositions of the prepared samples were evaluated using inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Blue Sop, Germany), and the results were summarized in Table 1.

Table 1
Actual chemical composition of the studied alloys (wt%).

Alloy Designation	Alloying Elements			
	Mg	Zn	Ca	Ag
ZX20	Bal.	2.00	0.20	-
ZXQ0.1	Bal.	2.07	0.20	0.11
ZXQ0.3	Bal.	2.00	0.20	0.27
ZXQ0.5	Bal.	2.04	0.17	0.50

2.2. Microstructural characterization

The microstructure of the samples was characterized using an optical microscope (OM) and a scanning electron microscope (SEM). Samples for OM observation were prepared following standard procedures, including grinding, polishing, and etching. The etchant consisted of 1 g oxalic acid, 1 g acetic acid and 150 ml distilled water. The metallographic observation was conducted using an Olympus-BX51M microscope. A Tescan Mira3 SEM coupled with an energy-dispersive X-ray spectroscopy (EDS) was utilized to investigate the microstructural characteristics and their corresponding chemical compositions.

X-ray diffraction (XRD) technique was utilized to determine the phase composition of the samples, both before and after the corrosion test, using a Rigaku D/MAX/2500VB diffractometer. The diffractometer was operated in the conventional θ - 2θ configuration, with a scanning rate of $1^\circ/\text{min}$ over a 2θ range of 20° to 80° .

The corrosion morphologies of the samples after 14 days' immersion in Hanks' solution were also evaluated using a 3D microscope with super depth of field (Keyence VHX-5000, Japan). Prior to observation, the corroded specimens were sequentially rinsed with chromic acid, acetone, ethanol, and distilled water to remove all corrosion products.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi to investigate the surface chemistry of the samples after the *in-vitro* corrosion test. The binding energy (BE) of the collected XPS spectra was calibrated by setting the C 1 s signal of the adventitious carbon (AC) at BE = 284.8 eV. The acquired spectra were analyzed using Avantage software to identify and quantify the surface elements and their chemical states.

2.3. Electrochemical test

The *in-vitro* corrosion properties of the samples in Hanks' solution, maintained at $37 \pm 1^\circ\text{C}$, were evaluated using electrochemical techniques. A conventional three-electrode cell was used, with the sample as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The exposed surface area of the sample in contact with the electrolyte was 1 cm^2 . The open circuit potential (OCP) of the sample was continuously monitored for 4 h to evaluate the corrosion tendency of the alloys in Hanks' solution. The potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) tests were conducted when a stable OCP had been reached. The PDP test was performed by sweeping the potential from -0.3 V to 0.3 V vs. OCP at a scan rate of 1 mV/s . The EIS test was carried out by applying a perturbation of 5 mV around the OCP, within a frequency range of 0.01 Hz to 10^5 Hz .

The corrosion current density, i_{corr} , of each sample was derived from the PDP curve using the Tafel extrapolation method. i_{corr} in A/cm^2 can be converted to the corrosion rate (CR) in mm/year using the following equation:

$$P_i = 22.85 i_{\text{corr}} \quad (1)$$

2.4. In-vitro immersion test

The degradation rate of the samples was also evaluated through an *in-vitro* immersion test in Hanks' solution at 37°C , following the guidelines of ASTM G31–72. The ratio between the surface area of the sample and the volume of the electrolyte was maintained at 1 cm^2 : 20 ml . Throughout the 168-hour immersion period, the evolution of the solution's pH and Mg^{2+} concentration was monitored. After the immersion test, the corrosion products on the sample surface were removed, and the weight change of the sample before and after immersion was measured. The corrosion rate was then calculated using the following equation:

$$P_w = \frac{K \bullet \Delta W}{A \bullet T \bullet D} \quad (2)$$

Where $K = 8.76 \times 10^4$ is a unit conversion constant, ΔW is the weight loss caused by the immersion, A is the exposed surface area of the sample in cm^2 , T is the immersion time in h, and D is the density of the sample in g/cm^3 .

2.5. Tensile test

The effect of degradation on the mechanical integrity of the studied alloys in Hanks' solution was evaluated via tensile testing according to ASTM E8 standards. Tensile specimens, with a 5 mm gauge length, were machined from as-extruded rods along the extrusion direction. After being immersed in Hanks' solution for specific durations, the samples were tested using a universal testing machine (Instron 3369) at a crosshead speed of 2 mm/s. To ensure reproducibility, three samples were tested for each condition.

3. Results and discussion

3.1. Microstructure characterization

The optical microstructures observed along the extrusion direction of the as-extruded alloys are shown in Fig. 1. It is evident that almost all the samples exhibit fine equiaxed grains, with a small fraction of larger grains. As confirmed in our previous work [12], the equiaxed grains had been formed through dynamic recrystallization, while the larger grains, elongated along the extrusion direction, are the residual deformed grains (as indicated by the yellow arrows in Fig. 1). Some secondary phases were also identified in the samples, appearing as dark contrast. These secondary phases are discontinuously aligned along the extrusion direction. The average grain size of all the alloys was measured to be approximately 7 μm , regardless of their Ag contents.

The microstructures of the as-extruded alloys were characterized using SEM, and the results are presented in Fig. 2. It is evident that the secondary phase particles are randomly distributed throughout the samples, with no preferential sites for their precipitation. However, larger particles are more commonly found at the triple junctions formed

by adjacent grains. The incorporation of Ag in the alloy did not induce significant changes in the characteristics of the secondary phases, except that their volume fraction appears to depend on Ag content, as shown in Fig. 3. Specifically, a slight addition of Ag (0.1 wt% and 0.3 wt%) to the ZX20 alloy increased the secondary phase fraction from 1.2 % to 1.3 % and 1.5 %, respectively. However, further increasing the Ag content to 0.5 wt% led to a decline in the fraction to 0.9 %. The particle size distribution is also affected by the Ag content in the alloy. As shown in Fig. 2, SEM analysis revealed that all alloys exhibited a similar maximum size of second-phase particles (measured by equivalent diameter, assuming a spherical geometry), approximately $11.01 \pm 0.45 \mu\text{m}$. Notably, the proportion of fine second-phase particles with an equivalent diameter below 1.5 μm increased with Ag addition, rising from 55 % in the ZX20 alloy to 79 % in the ZXQ0.5 alloy. This parameter reflects the refinement of second-phase particles rather than the grain size.

Apart from their distribution, the chemical compositions of the particles were also analyzed, and the results are presented in Table 2. It is evident that the secondary particles—such as the one labeled as 1# in the ZX20 alloy—contain significantly higher amounts of Zn and Ca than those added to the bulk alloy. In contrast, Region 2#, selected from the matrix, exhibits a chemical composition nearly identical to that of the alloy. A similar enrichment of alloying elements in the secondary precipitates is observed in the other three alloys, as confirmed by the chemical compositions of Regions 3#, 5#, 7#, and 9#. Specifically, the Zn content in Region 3# is more than ten times higher, while Ca and Ag are approximately 40 and 5 times higher, respectively, than their average concentrations in the alloy.

The phase compositions of the as-extruded alloys were characterized using XRD, and the results are shown in Fig. 4. All the alloys exhibited similar phase compositions, as indicated by their nearly identical XRD patterns. Peaks at $2\theta = 32.5^\circ, 34.8^\circ, 37.0^\circ$ and 48.2° correspond to the (10–10), (0002), (10–11), and (10–12) planes of $\alpha\text{-Mg}$, while peaks at $21.2^\circ, 31.6^\circ$ are attributed to the (200) and (300) planes of $\text{Ca}_2\text{Mg}_6\text{Zn}_3$. Both phases were present in all alloys, regardless of Ag content. However, the relative intensity of the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ peaks decreased with increasing Ag content and became barely detectable in the ZXQ0.5 alloy due to its reduced volume fraction, as shown in Fig. 3.

Moreover, the relative intensity of the Mg (0002) peak is the weakest

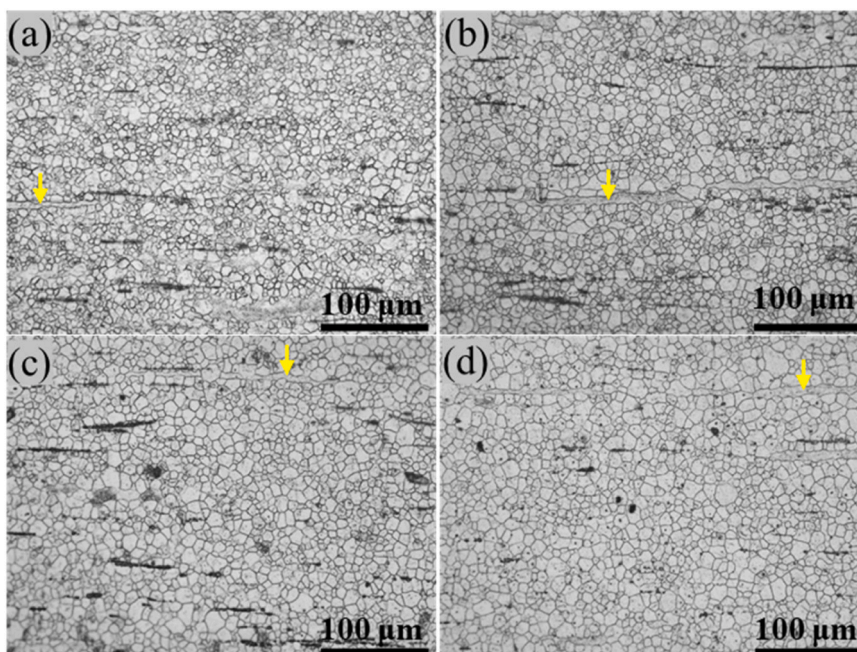


Fig. 1. Optical microstructure of the as-extruded alloys: (a)ZX20; (b)ZXQ0.1; (c) ZXQ0.3; (d) ZXQ0.5.

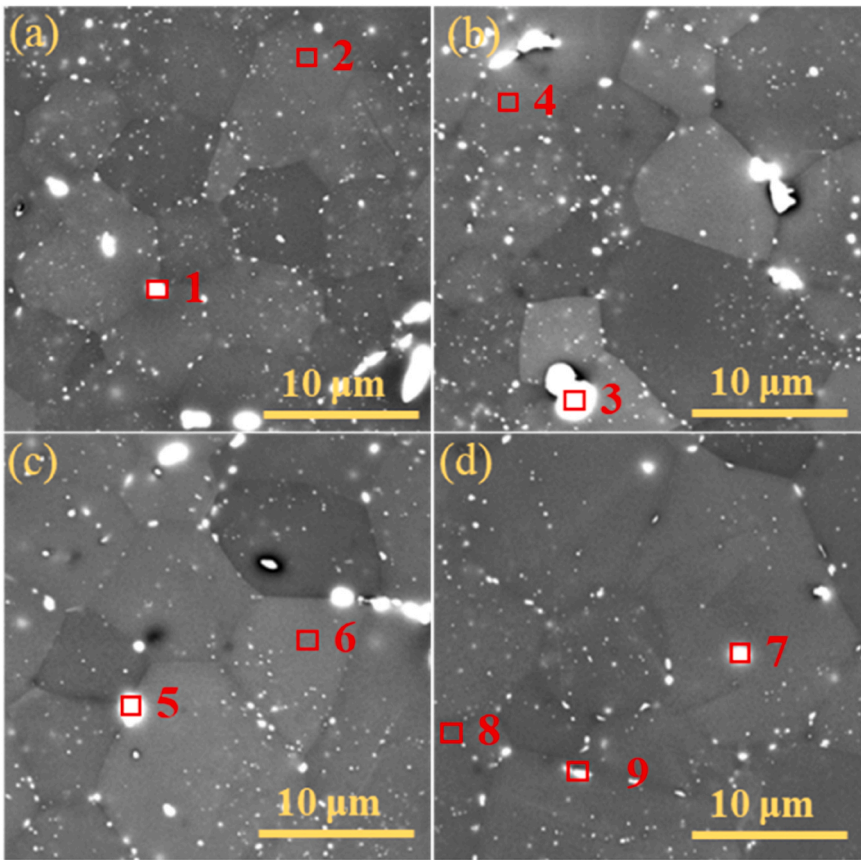


Fig. 2. SEM image and EDS mapping results of the as-extruded alloys observed in transverse direction : (a) ZX20 alloy; (b) ZXQ0.1 alloy; (c) ZXQ0.3 alloy; (d) ZXQ0.5 alloy.

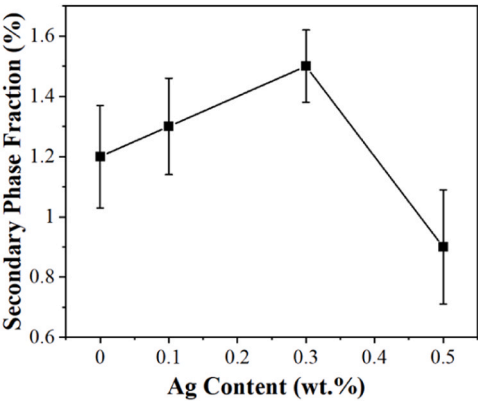


Fig. 3. Dependence of the volume fraction of secondary phases on the Ag content in the as-extruded alloys.

compared to the Mg (10–10) and Mg (10–11) peaks, which deviates from the theoretical expectation where Mg (0002) should be the second

strongest. This discrepancy may be attributed to the preferential grain orientation in the as-extruded alloys, suggesting that the basal planes are aligned parallel to the extrusion direction.

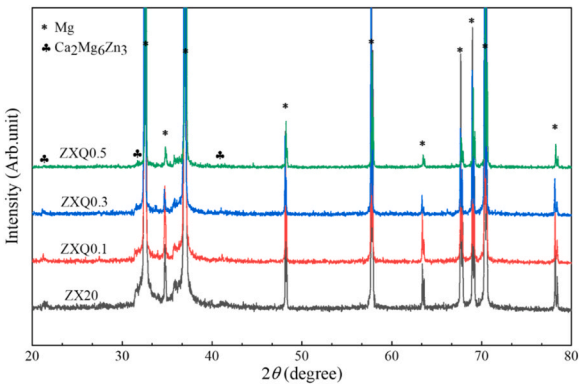


Fig. 4. XRD patterns of the as-extruded alloys.

Table 2
The chemical compositions of the characteristic sites marked in Fig. 2 (wt%).

Element	ZX20		ZXQ0.1		ZXQ0.3		ZXQ0.5		
	1#	2#	3#	4#	5#	6#	7#	8#	9#
Mg	82.5	97.7	62.8	97.2	75.3	97.4	91.5	94.8	84.9
Zn	13.8	2.1	27.3	2.6	18.2	2.1	6.1	3.9	1.8
Ca	3.7	0.2	8.9	0.2	5.1	0.0	1.6	0.5	12.9
Ag	0.0	0.0	1.0	0.0	1.5	0.4	0.8	0.9	0.4

3.2. In vitro immersion test

Immersion of Mg alloys in Hanks' solution induces significant corrosion following the reactions:

Anodic reaction :



Cathodic reaction :



Overall reaction:



As a result, several phenomenological changes may occur, including weight loss, solution alkalization (due to H_2 evolution), and the release of Mg^{2+} ions into the solution. These degradation byproducts have raised ongoing concerns over the feasibility of Mg-based implants. On the other hand, these factors serve as key indicators of the corrosion performance of the studied samples and are presented in Fig. 5.

Fig. 5(a) presents the pH evolution of the solutions throughout the immersion process, where two distinct stages can be identified. The first stage is characterized by an approximately linear increase in pH with immersion time, where the pH of the solution rapidly increased to ~ 8.7 within the first 12 h. During this initial stage, the pH curves for all samples were nearly identical. However, as the immersion time increased, significant differences emerged in the pH evolution. The curves for the ZX20 and ZXQ0.1 alloys remained almost the same and were consistently lower by approximately 0.33 compared to the coinciding curves of the ZXQ0.3 and ZXQ0.5 alloys. After 168 h of immersion, the pH of the solution containing the ZX20 and ZXQ0.1 alloys increased to 9.23, whereas the pH of the solutions with the ZXQ0.3 and ZXQ0.5 alloys rose to a higher value of 9.57, indicating more severe corrosion in the latter two alloys.

The evolution of Mg^{2+} concentration ($C_{\text{Mg}^{2+}}$) follows similar trend to that of the pH evolution over immersion time, as shown in Fig. 5(b). The initial $C_{\text{Mg}^{2+}}$ in the fresh Hanks' solution was 6.0 mg/L, which increased as corrosion progressed. During the initial stage, $C_{\text{Mg}^{2+}}$ climbed rapidly, reaching approximately five times the initial value, indicating a rapid release of Mg^{2+} from the sample surface. However, the increasing rate slowed with the prolonged immersion. Specifically, the $C_{\text{Mg}^{2+}}$ of the ZX20 and ZXQ0.1 alloy increased marginally to 40.8 mg/L between 12 and 168 h of immersion. In contrast, the ZXQ0.3 and ZXQ0.5 alloy had released more Mg^{2+} in the solution, resulting in final $C_{\text{Mg}^{2+}}$ values of 53.89 mg/L and 49.31 mg/L, respectively.

Both the pH and $C_{\text{Mg}^{2+}}$ evolution suggest that the corrosion process of the samples in Hanks' solution can be divided into two distinct stages. In the initial stage, corrosion occurred immediately upon immersion at a dramatic rate, with negligible differences among the samples. However, in the later stage, the corrosion rate slowed significantly, with the degree of retardation varying depending on the alloy composition. This reduction in the corrosion rate is likely due to the formation of a corrosion product layer on the sample surface, which may have inhibited mass transfer, thereby limiting the progression of the corrosion process.

On the other hand, the mild alkalization of the solution and the increased Mg^{2+} concentration is not expected to cause serious adverse effects on the human body. Studies have shown that an alkaline environment can promote bone tissue regeneration and support cell survival [25–28]. Comparable or even enhanced cell activity and bone regeneration have been reported in solutions with a pH of approximately 9.0, compared to the reference pH of 7.4. In this context, a pH of ~ 9.5 after 168 h of immersion remains acceptable, considering that pH value would be lower in the *in-vivo* conditions, where constant fluid flow would reduce local alkalization compared to the static *in-vitro* environment employed here. The maximum Mg^{2+} concentration tolerable by the human body is generally around 389 mg/L, which is roughly 16 times the normal physiological level [29]. This value is significantly

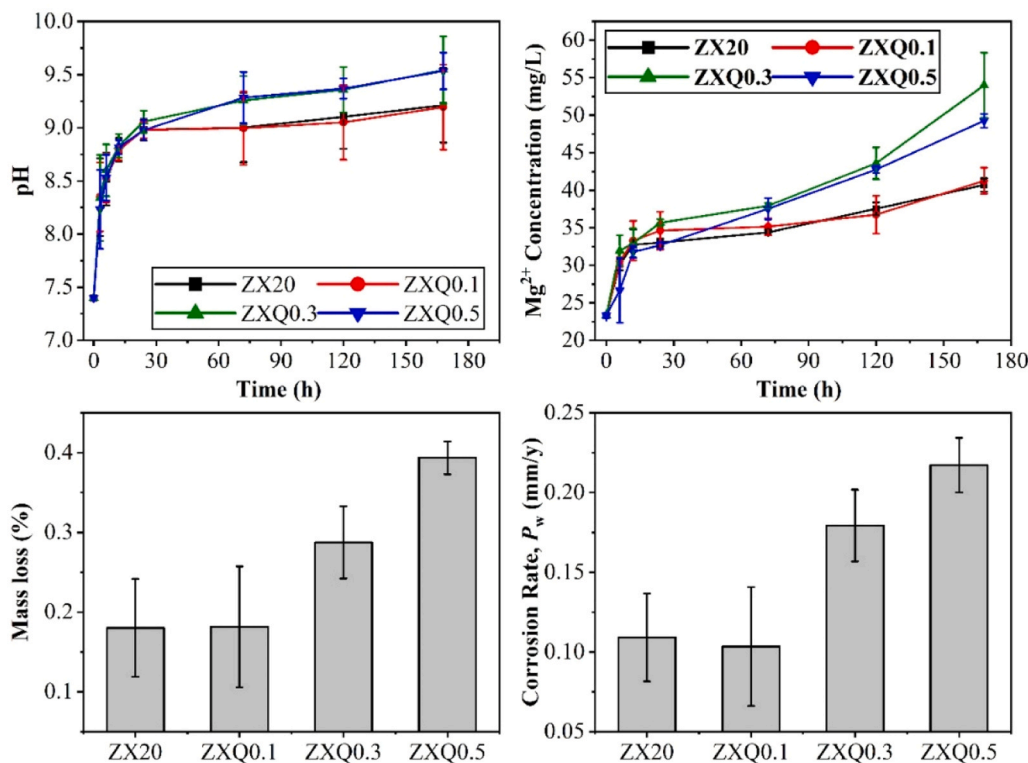


Fig. 5. (a) pH value, (b) Mg^{2+} concentration of the solution as well as the (c) weight loss and (d) corrosion rate of the as-extruded alloys after 168 h' immersion in Hanks' solution.

higher than the Mg^{2+} concentration measured after the immersion test in the present study. Therefore, both the pH and Mg^{2+} concentration remain within acceptable limits, mitigating concerns about corrosion-induced excessive alkalization and Mg^{2+} release.

The weight of the samples was carefully measured before and after the immersion test, and the corresponding weight loss is comparatively presented in Fig. 5(c). It is evident that a minor addition of 0.1 wt% Ag to the ZX20 alloy did not cause a significant change in weight loss during the immersion test, with approximately 0.18 % of the initial weight being lost. However, when the Ag content was increased beyond 0.3 wt %, the weight loss rose sharply to 0.28 % for 0.3 wt% Ag and further to 0.39 % for the alloy containing 0.5 wt% Ag. Based on the weight loss shown in Fig. 5(c), the corrosion rates of the studied alloys were calculated using Eq. (2), and the results are illustrated in Fig. 5(d). After 168 h' immersion, the average corrosion rates of the ZX20, ZXQ0.1, ZXQ0.3, and ZXQ0.5 alloys were measured at 0.11 mm/y, 0.10 mm/y, 0.18 mm/y, and 0.22 mm/y, respectively. Unsurprisingly, the evolution of the solution pH and Mg^{2+} concentration closely corresponded to the measured weight loss. The immersion tests indicated that the corrosion of the ZX20 alloy had been compromised by the addition of Ag. Nevertheless, the overall corrosion rate in Hanks' solution was significantly lower than that observed in NaCl electrolyte [12] and well below than that applicable for biomedical applications [30].

The degradation of the studied alloys in Hanks' solution resulted in distinct morphological changes depending on their Ag content, as shown in Fig. 6. During the first 12 h' immersion, hardly any traces of corrosion could be visibly detected, as indirectly evidenced by the marginal pH and $C_{Mg^{2+}}$ evolution shown in Fig. 5. Therefore, Fig. 6 presents the corrosion morphologies observed at longer immersion times. After 12 h of immersion, the ZX20 alloy exhibited noticeable and discrete black lines—indicative of corrosion—spreading across the sample surface (Fig. 6(a1)). With extended immersion to 24 h, the existing corrosion lines became more pronounced, and new lines also began to form (Fig. 6(a2)). Prolonging the immersion time to 72 h had left more corrosion lines decorated with some localized corrosion spots (Fig. 6(a3)). The propagation of corrosion appeared to be largely confined to the existing corrosion lines and spots, as extending the immersion time to 168 h did not result in significant morphological changes—apart from the affected areas becoming darker (Fig. 6(a5)). This suggests that the corrosion is progressing into deeper regions rather than spreading laterally.

The addition of Ag to the ZX20 alloy significantly affected its corrosion behavior. At an Ag content of 0.1 wt%, fewer corrosion lines formed on the ZXQ0.1 alloy surface after 24 h of immersion (Fig. 6(b2)) compared to the Ag-free ZX20 alloy, indicating an extended corrosion incubation period. However, as the immersion time increased beyond 72 h to 128 h, the corrosion appeared to accelerate, as evidenced by the

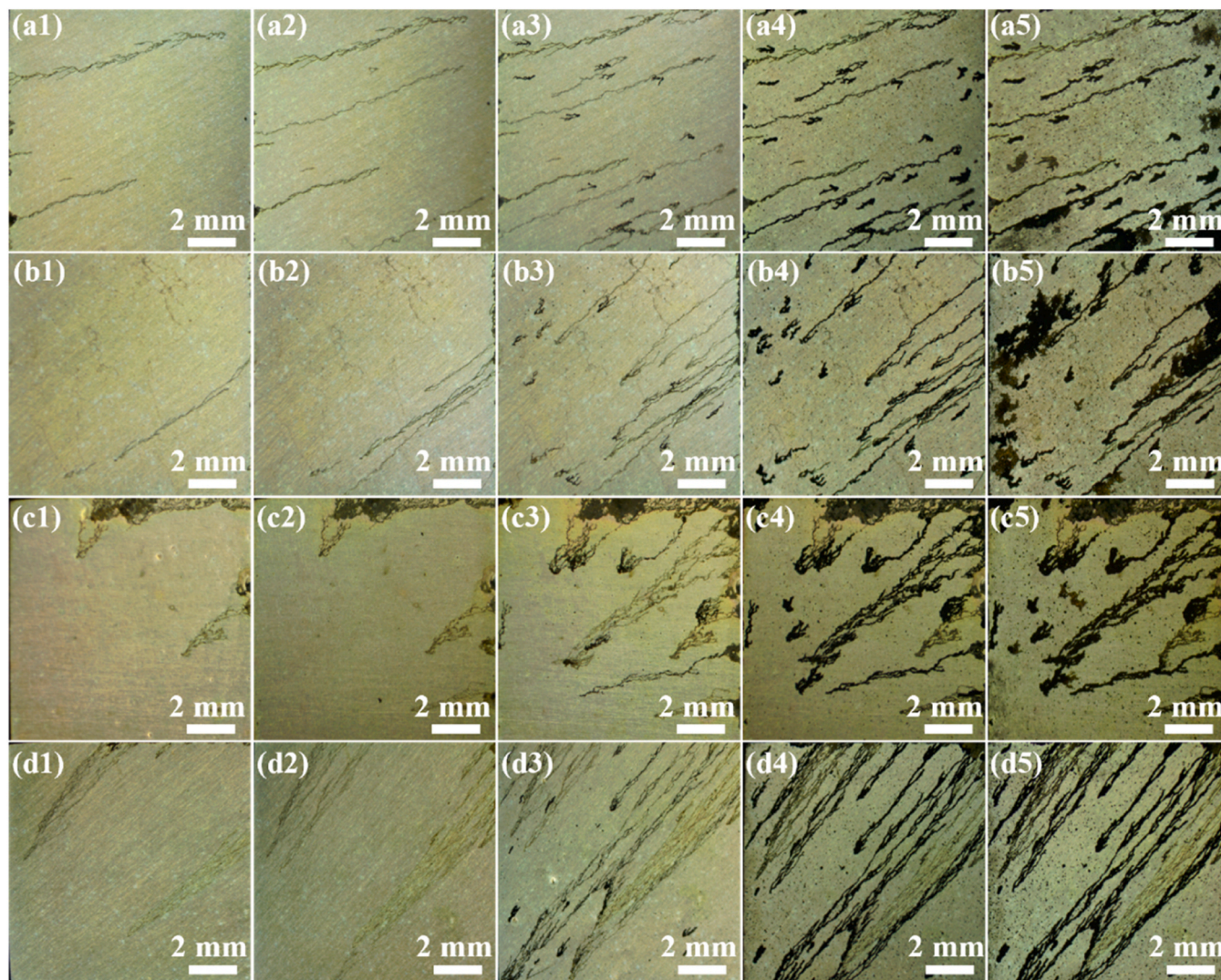


Fig. 6. Photos of the as-extruded (a1~a5) ZX20, (b1~b5) ZXQ0.1, (c1~c5) ZXQ0.3, (d1~d5) ZXQ0.5 alloys after immersion for (a1,b1,c1,d1) 12 h, (a2,b2,c2,d2) 24 h, (a3,b3,c3,d3) 72 h, (a4,b4,c4,d4) 120 h and (a5,b5,c5,d5) 168 h.

increased area fraction covered by corrosion products (Fig. 6(b5)). Increasing the Ag content to 0.3 wt% and 0.5 wt%, the surface of ZXQ0.3 and ZXQ0.5 alloys are also featured with corrosion lines and spots, and the area fraction of these features increased with the immersion time.

The fraction of the corroded area was calculated as an indicator of the corrosion progression, and the results are presented in Fig. 7. It is evident that the corroded area fraction increased with immersion time for all alloys. Among them, the Ag-free ZX20 alloy suffered the least corrosion, while the extent of corrosion showed a positive correlation with Ag content. The most severe corrosion was observed in the ZXQ0.5 alloy, with approximately 27.5 % of its surface affected after immersion for 168 h. The results shown in Fig. 7 correlate well with those presented in Fig. 5. However, it should be noted that corrosion propagation beneath the surface at the corrosion sites could not be assessed based solely on surface morphologies.

The corrosion morphologies were also observed using a 3D microscope with a super depth of field to evaluate the in-depth development of the corrosion process, and the results are presented in Fig. 8. The depth profiles extracted along the selected lines traversing the deepest corrosion pit on each sample are also included in Fig. 8. It is clear that all samples exhibited pitting corrosion with discrete surface pits, where maximum pit depth correlated with Ag content. Specifically, the maximum corrosion depth of the ZXQ0.1 alloy is measured to be approx. 300 μm , whereas the ZX20 and ZXQ0.3 present comparable max pitting depth of 272 μm and 289 μm , respectively. The ZXQ0.5 alloy, however, demonstrated the shallowest maximum pit depth of 93 μm . The depth profiles also confirmed the lateral corrosion propagation, evidenced by the pit coalescence in the ZXQ0.1 alloy where the deepest pit almost merged with the second deepest. This coalescence indicates the formation of thicker corrosion layers that can impede further corrosion, explaining why ZXQ0.1 shows slower overall degradation despite its deeper pits. In contrast, the ZXQ0.5 alloy exhibits shallower pits but a much larger corrosion surface fraction, leading to faster overall corrosion. In addition, the averaged corrosion depth of around 125 μm are measured from all the alloys with ≤ 0.3 wt% Ag if the max corrosion pit depth was excluded. These observations suggest that maximum pit depth alone does not directly determine the overall corrosion rate, which is also influenced by the lateral propagation of corrosion and the protective effect of corrosion product layers.

The evolution of corrosion rates with the immersion time primarily results from the gradual accumulation of corrosion products on the sample surface. Therefore, it is essential to investigate the morphologies as well as the chemical / phase compositions of the corrosion products. The corrosion morphologies of the samples after 7 days' immersion in the Hanks' solution was examined using SEM, as shown in Fig. 9. The samples experienced extensive corrosion, forming flocculent corrosion

products that partially covered sample surfaces, with coverage fraction increasing with Ag content. Beneath these flocculent deposits, typical mud-cracking morphology was observed from the alloys containing ≤ 0.3 wt% Ag. The flocculent products were so predominant on the ZXQ0.5 alloy that they obscured the substrate, preventing clear identification of mud-cracks (Fig. 9(m,n)). The mud-cracking morphology resulted from dehydration of corrosion products during SEM imaging under vacuum conditions.

Elemental mapping analysis was conducted, with results presented in Fig. 10. Mg, Ca, P, and O were detected across the sample surface, though each exhibited distinct distribution patterns. Ca and P were predominantly localized in flocculent deposits, whereas Mg was primarily concentrated in mud-cracked regions uncovered by flocculent deposits. Oxygen distribution appeared relatively uniform across the surface. Table 3 lists the concentration of each element detected on the corroded sample surface. It is clear that higher concentrations of Ca and P were deposited on the surface of the samples with Ag addition. The atomic ratio of Ca:P was in the range of 1.2–1.4, suggesting the deposition of Ca-P compounds during the immersion process. It can be predicted that Ca and P in the Hanks' solution were directly deposited on the sample surface, without participating in corrosion-related redox reactions. The increased predominance of Ca- and P-containing flocculent implies that Ag addition in the bulk alloy facilitated the Ca-P compounds deposition. The deposition of Ca-P compounds is generally considered beneficial for promoting bone adhesion after implantation [31–33].

The cross-sectional corrosion morphologies of samples immersed in Hanks' solution for 168 h were examined using SEM (Fig. 11) to reveal the accumulation of corrosion products. For clarity, representative localized regions containing the deepest corrosion pits are shown at higher magnification. The corrosion layers on ZX20 and ZXQ0.1 alloys appear largely uniform, with occasional pits only visible at higher magnifications. However, when Ag content increased to 0.3 wt% and 0.5 wt%, corrosion pits became readily observable at lower magnifications, indicating more severe pitting corrosion. Maximum pitting depths were measured as 46 μm (ZX20), 42 μm (ZXQ0.1), 136 μm (ZXQ0.3), and 40 μm (ZXQ0.5). Notably, while the maximum pitting depth for ZXQ0.5 (40 μm) is comparable to ZX20 and ZXQ0.1, its pit width exceeds 100 μm , facilitating identification. Moreover, two distinct regions are evident in the cross-sectional corrosion morphology: an inner layer characterized by mud-cracking and dark contrast, and an outer region exhibiting lighter contrast. This layered structure becomes more distinct when chemical distributions across the cross-section are mapped, as revealed in Fig. 11(e).

It is clear that the inner layer is mainly comprised of Mg and O, while Ca, P and O are concentrated on the outer layer. This stratified chemical distribution confirms Ca-P compounds deposit on the corrosion products rather than within them, consistent with surface morphology observations (Fig. 9). The concentrations of each element were semi-quantitatively analyzed using EDS, and the results are summarized in Table 4. The appreciable C content detected originated from the C-sputtering process prior to the SEM observation, therefore it is not related to the immersion corrosion process in any way. The selected point #1 from the outer region of the ZX20 alloy mainly contains O, P, Ca and Mg, with the atomic ratio of Ca:P = 1.08. As for the inner region (#3), only marginal amount of Ca and P was detected, and O and Mg dominates such inner region. Similar chemical distribution was also identified in the corrosion products of the Ag-containing alloy (e.g. ZXQ0.5), where the outer regions (#4) features a high content of Ca (8.1 at%) and P (7.0 at%), yielding a Ca:P ratio of 1.16. In the inner regions, the atomic ratio of Mg:O is approx. 0.5, indicating the formation of $\text{Mg}(\text{OH})_2$ in the corrosion process. In the outer regions, however, the majority of O is compounded with Ca and P to form calcium phosphates.

The phase compositions of the corroded surface were identified using the XRD technique, and the results are displayed in Fig. 12. Since the corrosion products accumulated at a rather slow rate to yield sufficient

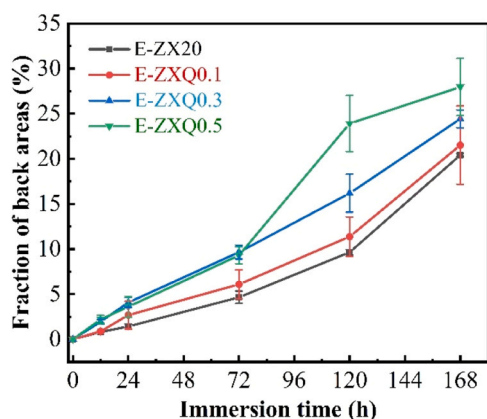


Fig. 7. Evolution of the corrosion area fraction of the studied alloys during immersion in Hanks' solution at $37 \pm 1^\circ\text{C}$.

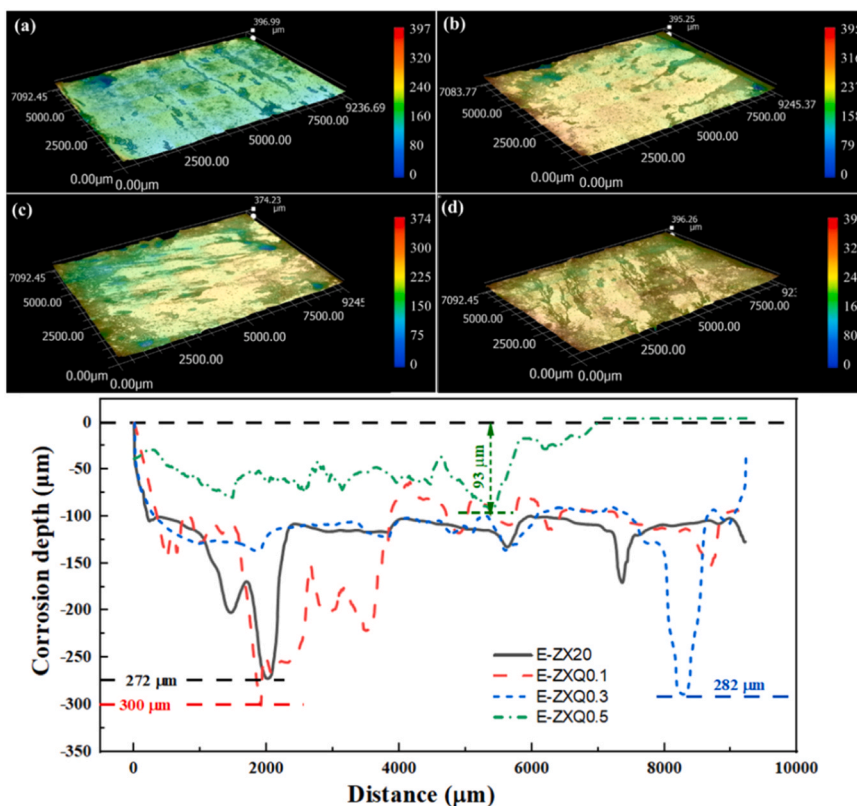


Fig. 8. 3D tomographic maps of (a) ZX20, (b) ZXQ0.1, (c) ZXQ0.3 and (d) ZXQ0.5 alloy after 14 days' immersion in Hanks' solution, and (e) the corresponding corrosion depth profiles along selected lines.

amount for XRD detection, the samples had been immersed in the Hanks' solution for an extended period (28 days). The XRD patterns were dominated by strong peaks corresponding to the bulk alloy matrix (α -Mg phase), which can be attributed to either the presence of a thin corrosion film or its partial coverage of the sample surface. In addition to the α -Mg peaks, diffraction peaks were observed at $2\theta = 18.5^\circ$, 37.9° , 50.76° , 58.6° , corresponding to the (001), (011), (012) and (110) planes of the crystalline $\text{Mg}(\text{OH})_2$. This indicates that $\text{Mg}(\text{OH})_2$ is the predominate corrosion product during the degradation of the alloy in the Hanks' solution. Furthermore, the intensity of the $\text{Mg}(\text{OH})_2$ peaks with respect to that of the α -Mg increased with higher Ag content in the alloy, suggesting more severe degradation of the Ag-containing alloy. For the alloy without any Ag addition, hardly any $\text{Mg}(\text{OH})_2$ peaks can be identified in the XRD profile. In addition, although Ca-P compounds were observed in the surface and cross-sectional morphologies, they were not detected in the XRD tests, likely due to their low deposition rate, discontinuous distribution and insufficient amount.

To identify the Ca- and/or P-containing compounds, the surface chemistry of the corroded sample was also analyzed using XPS. Fig. 13 shows the XPS spectra collected from the surfaces of the studied alloys after 28 days of immersion in Hanks' solution. The C 1s peaks of all alloys exhibit similar characteristics. Peak deconvolution reveals that each C 1s peak can be fitted into three sub-peaks at binding energies (BE) of 284.8 eV, 286.1 eV, and 288.5 eV. The sub-peak at 284.8 eV corresponds to adventitious carbon (AC) from airborne hydrocarbon contamination, while the sub-peak at 288.5 eV indicates the formation of metal carbonates (CO_3^{2-}) on the sample surfaces [34].

All samples display a single, well-defined Gaussian-symmetric peak in the Mg 1s spectrum, though peak positions vary significantly. The Mg 1s BE values for ZX20 and ZXQ0.1 alloys are nearly identical. However, as the Ag content increases, the Mg 1s peak shifts toward higher BE, suggesting altered valence states of Mg. Deconvolution resolves the Mg 1s peak into two sub-peaks at 1303 eV and 1305 eV, corresponding to

MgO and MgCO_3 , respectively [34]. The MgO component likely originates from dehydration of $\text{Mg}(\text{OH})_2$ (formed during immersion) under XPS vacuum conditions. The presence of MgCO_3 is further corroborated by the C 1s sub-peak at 288.5 eV. With increasing Ag content, the relative intensity of the Mg 1s sub-peak at 1305 eV (MgCO_3) progressively increases, indicating a higher proportion of MgCO_3 in the corrosion products. This is attributed to accelerated corrosion rates induced by higher Ag content (Fig. 5), generating more corrosion products. Notably, XPS only probes the extreme surface (several nanometers); thus, the trace surface MgCO_3 was undetectable by bulk XRD analysis (as mentioned in Fig. 12). The O 1s spectra of all samples deconvolute into two sub-peaks at 531.1 eV and 532.1 eV, corresponding to metal oxides and metal carbonates, respectively [34]. This aligns with the chemical states of Mg observed on the surface.

While the XPS survey spectra confirmed abundant Ca and P on the corrosion product surfaces, high-resolution scans (Ca 2p, P 2p) were performed to elucidate their chemical states. The P 2p peaks of all samples are consistent, appearing as a single peak between 130 and 136 eV with approximate Gaussian symmetry. According to P 2p orbital splitting rules, this peak comprises two spin-orbit components: P 2p_{3/2} and P 2p_{1/2}, with a fixed intensity ratio of 2:1 and energy separation of $\Delta\text{BE} = 0.87$ eV. Constrained fitting reveals a P 2p_{3/2} BE of 133.0 ± 0.1 eV for all samples, confirming the presence of phosphate ions (PO_4^{3-}) [34]. Similarly, the Ca 2p spectra deconvolute into Ca 2p_{3/2} and Ca 2p_{1/2} sub-peaks ($\Delta\text{BE} = 3.5$ eV). All samples exhibit two sets of Ca 2p_{3/2} sub-peaks at 347.0 eV and 347.7 eV. The sub-peak at 347.0 eV corresponds to CaCO_3 , while the 347.7 eV sub-peak is assigned to $\text{Ca}_3(\text{PO}_4)_2$ [34]. However, the observed BE (347.7 eV) deviates from the standard value for stoichiometric $\text{Ca}_3(\text{PO}_4)_2$ (345.5 eV), likely due to variations in Ca/P ratios and the presence of multiple calcium phosphate compounds with indistinguishable Ca 2p_{3/2} BE values. It should be noted that the valence states of Ca and P on the sample surface did not present any significant difference among all the studied samples,

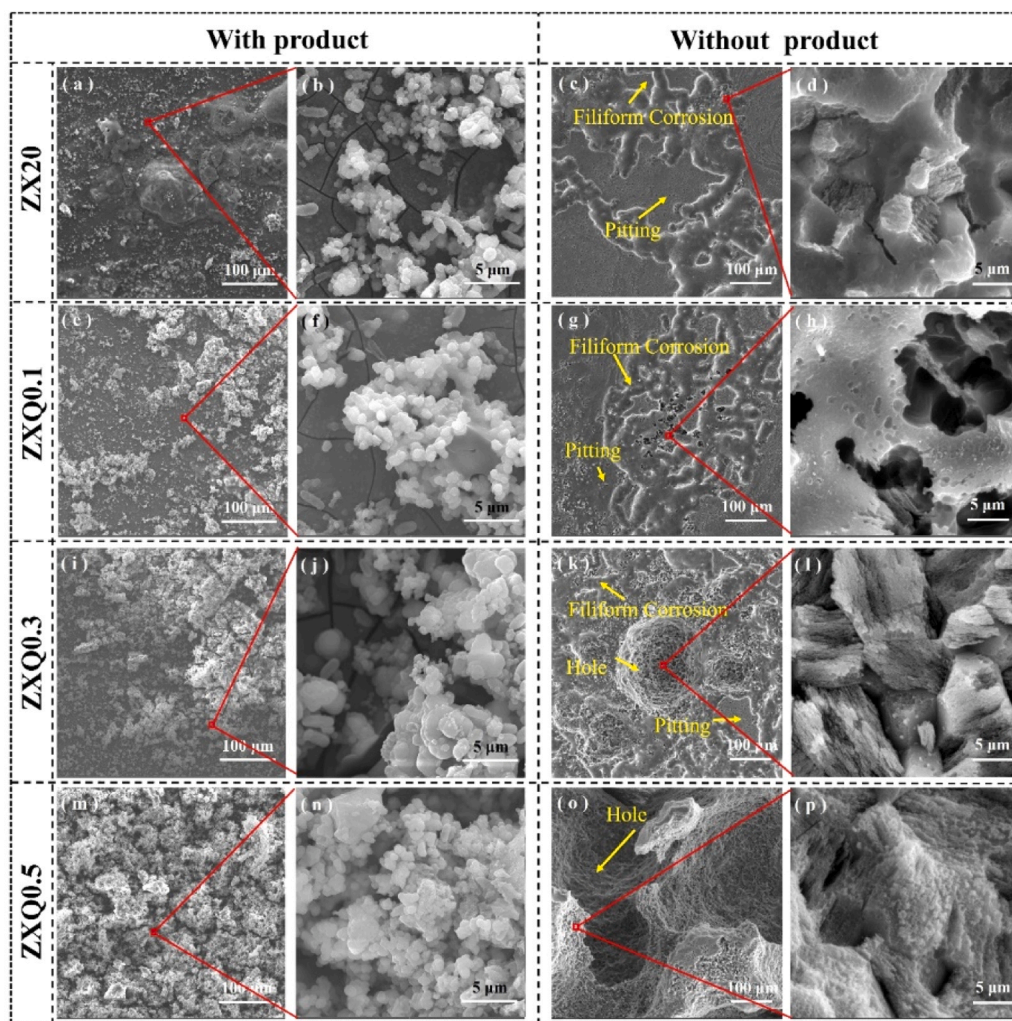


Fig. 9. SEM images of the studied alloys after immersion in Hanks' solution for 168 h at $37 \pm 1^\circ\text{C}$.

regardless of their bulk Ag content.

3.3. Electrochemical measurement

The open circuit potentials (OCP) of the Mg-2Zn-0.2Ca-xAg ($x = 0, 0.1, 0.3$ and 0.5 wt%) alloys during immersion in the Hanks' solution at $37 \pm 1^\circ\text{C}$ were continuously recorded, and the results are exhibited in Fig. 14(a). It is evident that the OCPs of all the samples increased immediately upon the start of the immersion test, suggesting the rapid passivation of the sample surface. The initial passivation durations varied depending on the Ag contents, i.e., about 1000 s for the ZX20 alloys and 500 s for the rest three Ag-containing alloys. Furthermore, the extent of passivation was also influenced by the Ag content. To be specific, the OCP of ZX20 alloy increased to around -1.64 V vs. SCE within the initial passivation stage, whereas the OCPs for the ZXQ0.1, ZXQ0.3 and ZXQ0.5 alloys are -1.64 V, -1.58 V, and -1.61 V vs. SCE, respectively, suggesting that Ag addition promotes passivation of the ZX20 alloy. Immediately after the initial passivation, the OCP evolution curve present a characteristic serrated pattern due to the competing passivation and activation occurring on the sample surface. The serrated OCP curve indicate that the passivation layer formed are not sufficiently protective for the alloy. Overall, the passivation process outweighed the activation process, as confirmed by the increased OCPs of the alloy, except for the ZXQ0.3 alloy where its OCP fluctuates around -1.60 V vs. SCE during the entire immersion. Finally, the OCPs of all the samples stabilized, around -1.61 V vs. SCE for the ZX20 and ZXQ0.1 alloys and

-1.60 V vs. SCE for the ZXQ0.3 and ZXQ0.5 alloys, even though with apparent spikes on their curves, suggesting the balance of passivation and activation had been reached. Moreover, a slightly nobler final OCPs were recorded for the Ag-containing alloys, indicating that they may be less susceptible to corrosion from the thermodynamic perspective.

The *in-vitro* corrosion performance of the alloys in Hanks' solution was evaluated using the potentiodynamic polarization (PDP) technique, and the resulting PDP curves after 12 h' immersion are shown in Fig. 14 (b). Corrosion potential, E_{corr} , and corrosion current density, i_{corr} , were derived from these curves. It is evident that the Ag-containing alloys exhibited higher E_{corr} values other than the ZX20 alloy, consistent with the OCP results (Fig. 14(a)) and that published in the literature [19,24], suggesting that Ag addition reduces thermodynamic driving force for corrosion. The cathodic branches of the PDP curves exhibited similar behavior (despite differences in their coordinates), indicating comparable cathodic reaction kinetics during the corrosion process. However, the anodic branches showed distinct characteristics for each sample. It is obvious that the current density of all the samples increases with increasing overpotential, though along different paths. Specifically, steep anodic branches were observed, i.e., when the samples (except for the ZXQ0.1 alloy) were slightly polarized anodically away from the free corrosion potential, the current density increased only slightly over a significant potential range. This behavior is attributed to passivation by the accumulation of corrosion products on the sample surface. Upon further polarization, the current density increased dramatically, even with minimal potential changes. The transition point to separate the two

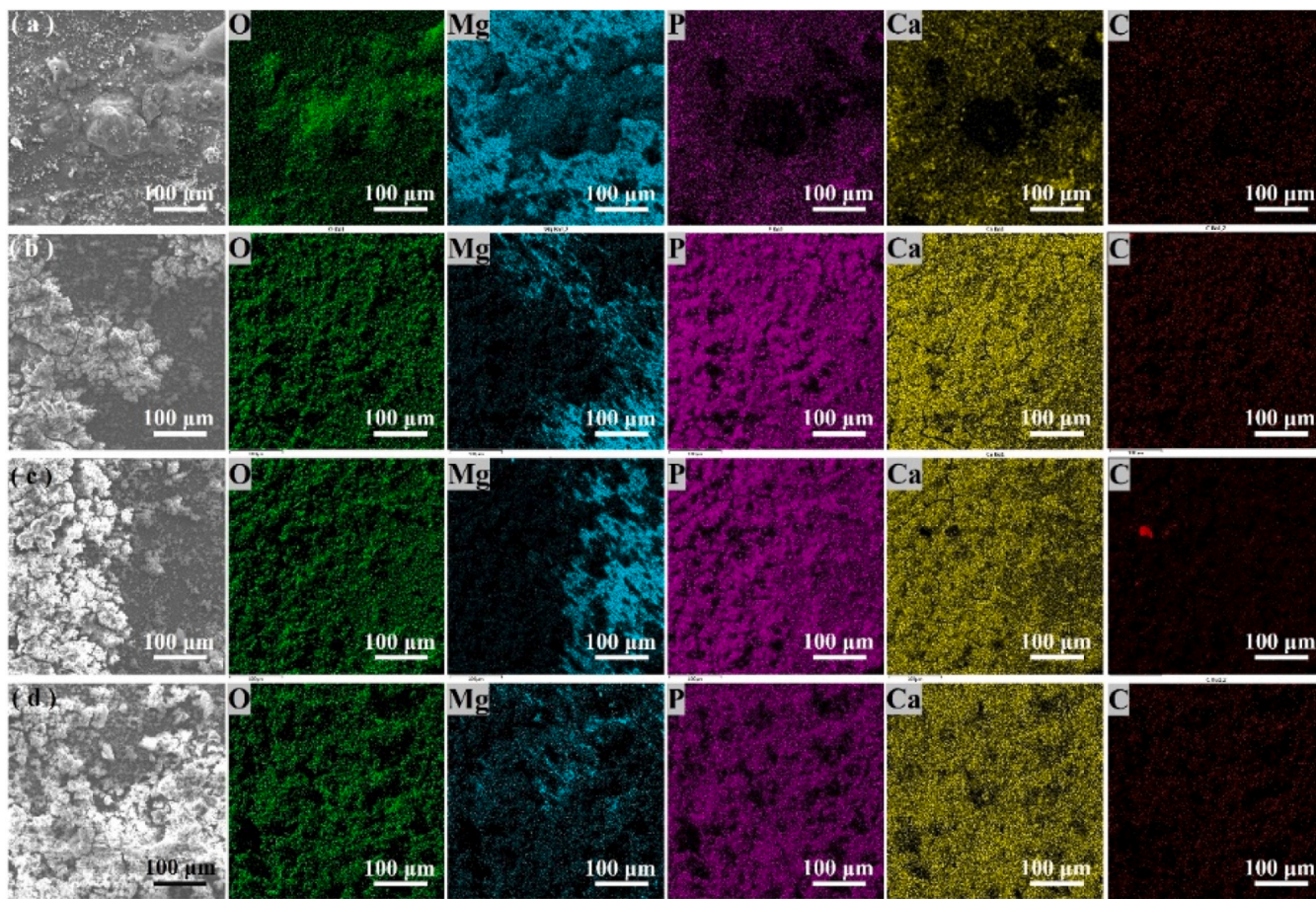


Fig. 10. Elemental mapping analysis of the samples after immersion in Hanks' solution for 168 h, (a) ZX20, (b) ZXQ0.1, (c) ZXQ0.3 and (d) ZXQ0.5.

Table 3

The chemical analysis of the corroded sample surface.

Sample ID	Elemental Concentration (at.%)				
	Mg	O	Ca	P	C
ZX20	32.2	43.8	3.0	2.7	18.3
ZXQ0.1	8.0	55.2	12.6	9.3	14.9
ZXQ0.3	10.1	52.1	12.3	8.9	16.6
ZXQ0.5	5.0	57.8	13.4	9.5	14.3

regions on the anodic branch is designated as E_{break} , and is critical for evaluating the protective ability of the corrosion products formed on the sample surface [32]. In contrast, the ZXQ0.1 alloy did not exhibit any passivation. Its current density increased by more than two orders of magnitude with only slight polarization, and two transition points were observed on its anodic branch at 0.01 V and 0.13 V vs. OCP. As shown in Fig. 14(b), the E_{break} values for the ZX20, ZXQ0.1, ZXQ0.3, and ZXQ0.5 alloys were 0.13 V, 0.01 V, 0.04 V, and 0.12 V, respectively, relative to their respective OCPs. Therefore, from a thermodynamic perspective, the ZX20 and ZXQ0.5 alloys are expected to exhibit better corrosion resistance.

Since none of the anodic branches in the PDP curves (Fig. 14(b)) exhibited a reliable Tafel region, the corrosion current densities of the alloys were determined by applying Tafel extrapolation exclusively to the cathodic branches, where well-defined Tafel behavior was observed. The results are summarized in Table 5. The four samples exhibit similar cathodic Tafel slopes, ranging from 218 to 248 mV/decade, which are in good agreement with values reported in the literature [35]. Therefore, it can be inferred that identical cathodic reactions were involved in the

corrosion process. A corrosion current density of $2.68 \mu\text{A}/\text{cm}^2$ was measured for the Ag-free ZX20 alloy. A minimal addition of 0.1 wt% Ag slightly reduced the i_{corr} value to $2.10 \mu\text{A}/\text{cm}^2$. However, increasing the Ag content to 0.3 wt% and 0.5 wt% appeared to compromise corrosion resistance, with i_{corr} values rising to $5.93 \mu\text{A}/\text{cm}^2$ and $3.51 \mu\text{A}/\text{cm}^2$, respectively. These i_{corr} values had been converted into corrosion rate in mm/y based on Eq. (1), as tabulated in Table 5.

Although the trend of corrosion rate as a function of Ag content generally agrees with that derived from weight loss measurements (Fig. 5(d)), the absolute values show notable discrepancies. Both Equation (1) and Eq. (2) are based on the simplified assumption of uniform corrosion, where the total weight loss or corrosion current is normalized by the exposed sample surface area. Nevertheless, the actual corrosion morphologies as shown in Fig. 6 contradict this assumption. Therefore, the discrepancies in corrosion rates are primarily attributed to the non-uniform nature of the corrosion process.

The EIS diagrams of the studied alloys after 12 h of immersion in Hanks' solution are shown in Fig. 15. All samples yielded similar Nyquist plots (Fig. 15(a)), characterized by suppressed capacitive semicircles at frequencies above approximately 0.04 Hz and inductive loops at lower frequencies. However, the diameters of the semicircles vary significantly depending on the Ag content of the alloys. Notably, the Nyquist plot of the ZX20 alloy expanded markedly with the addition of 0.1 wt% Ag. Despite this, the semicircle size does not increase monotonically with higher Ag content. Further increases to 0.3 wt% and 0.5 wt% Ag resulted in the smallest and second smallest semicircles, respectively, among the four alloys studied. A larger Nyquist plot generally suggests better corrosion resistance [32,36]. In this regard, the lowest corrosion rate of the ZXQ0.1 alloy could be inferred, which is also in consistent with the PDP analysis.

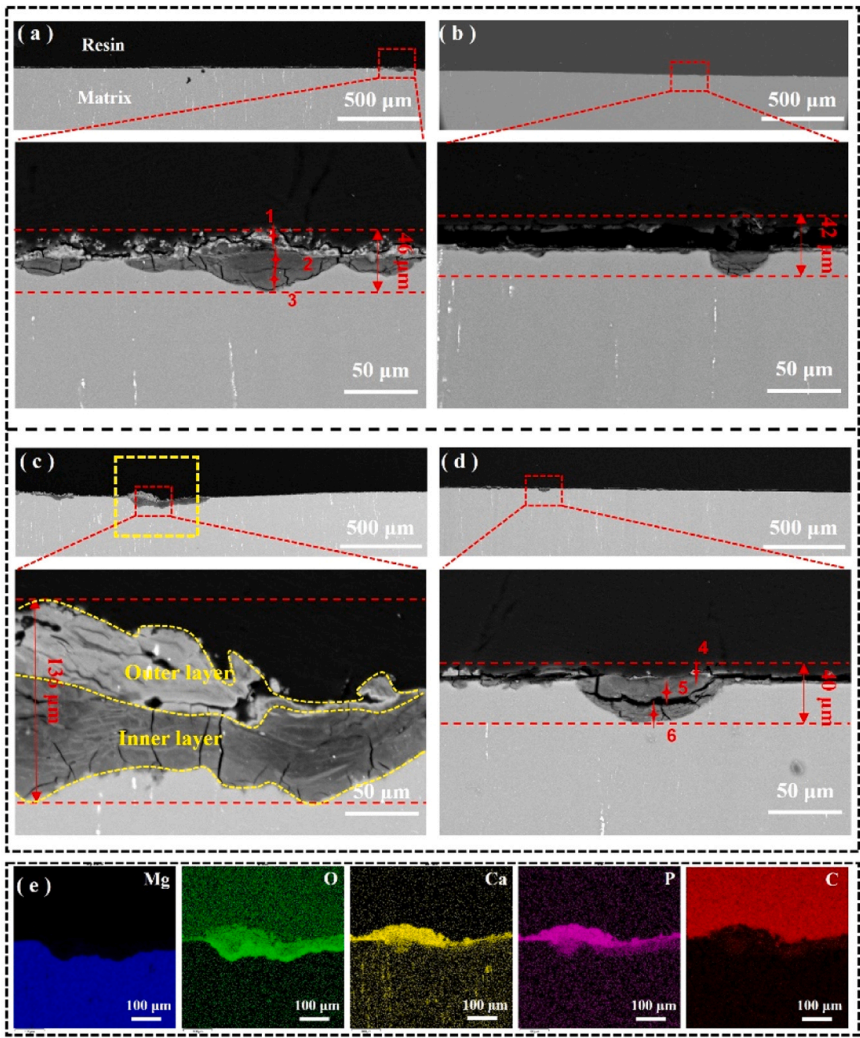


Fig. 11. Cross-sectional corrosion morphologies of (a) ZX20, (b) ZXQ0.1, (c) ZXQ0.3 and (d) ZXQ0.5 alloy after immersion for 168 h in Hanks' solution and (e) the resulting elemental distribution of the ZXQ0.3 alloy.

Table 4
EDS results of the marked points in Fig. 11 (at.%).

Element	ZX20			ZXQ0.5		
	1	2	3	4	5	6
O	54.1	37.3	47.6	40.2	48.4	52.7
Mg	4.8	12.1	25.1	3.7	20.1	23.9
C	26.0	48.1	25.2	40.7	23.7	22.4
P	7.2	1.3	0.6	7.0	4.3	0.4
Ca	7.8	0.6	0.5	8.1	2.7	0.1
Zn	0.1	0.5	0.9	0.1	0.6	0.4
Ag	-	-	-	0.1	0.1	0.2
Ca/P	1.08	0.46	0.83	1.16	0.63	0.25

Nevertheless, although the Nyquist plots appear similar, they can be more clearly interpreted by examining the corresponding phase angle Bode plots. The Bode plot of the ZX20 alloy exhibits two distinct peaks within the frequency range of 10^4 Hz to 0.04 Hz (Fig. 15(b)), indicating that the suppressed capacitive semicircle observed in this range actually originates from two separate capacitive behaviors. However, around the transition frequency of approximately 200 Hz, these two capacitive responses may become superimposed, making them difficult to distinguish in the Nyquist diagram.

The superimposition of two capacitive loops can also be identified in the Bode phase angle plots of the ZXQ0.1 and ZXQ0.5 alloys. However,

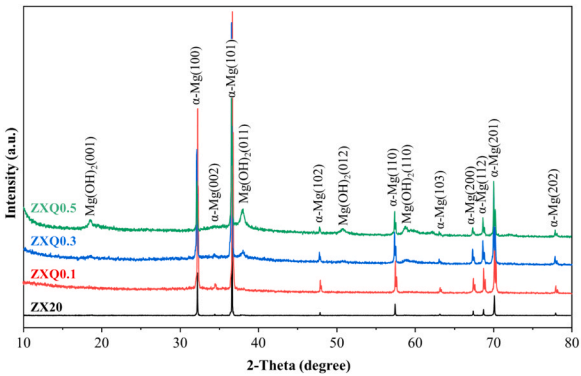


Fig. 12. XRD patterns of the studied alloys after immersion in Hanks' solution at $37 \pm 1^\circ\text{C}$ for 28 days.

for the ZXQ0.5 alloy, the phase angle peak at frequencies above 200 Hz is significantly flattened, while for the ZXQ0.1 alloy, it is shifted toward a higher frequency range. In contrast, the ZXQ0.3 alloy exhibits a distinctly different Bode plot, showing only a single phase-angle peak in the frequency range above 0.04 Hz. These observations suggest that Ag addition influences the corrosion process by affecting either the charge transfer or mass transfer mechanisms. All the samples except the ZXQ0.3

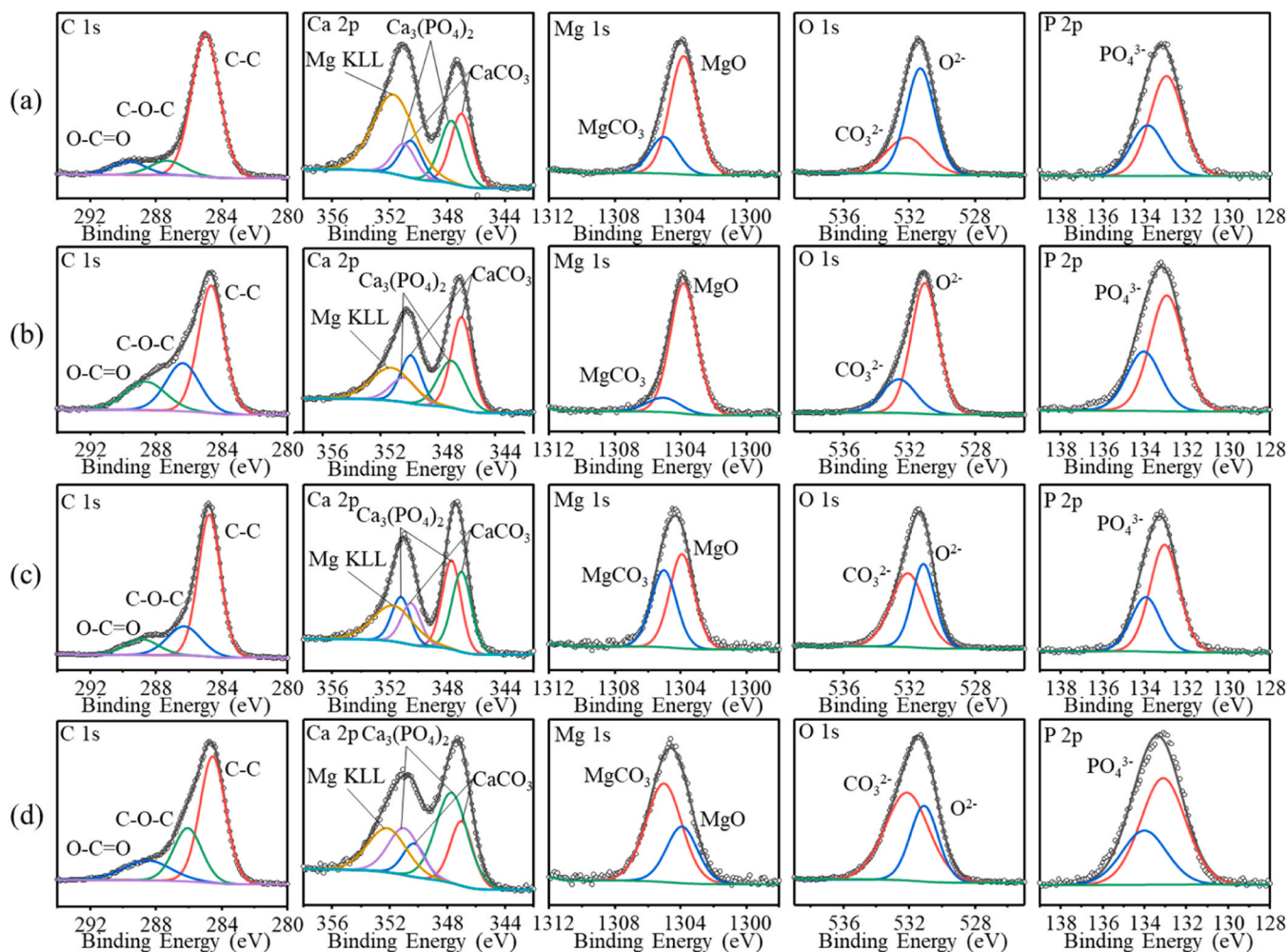


Fig. 13. The XPS spectra collected from the sample surface after 28 days' immersion in Hanks' solution at $37 \pm 1^\circ \text{C}$, (a) ZX20, (b) ZXQ0.1, (c) ZXQ0.3 and (d) ZXQ0.5.

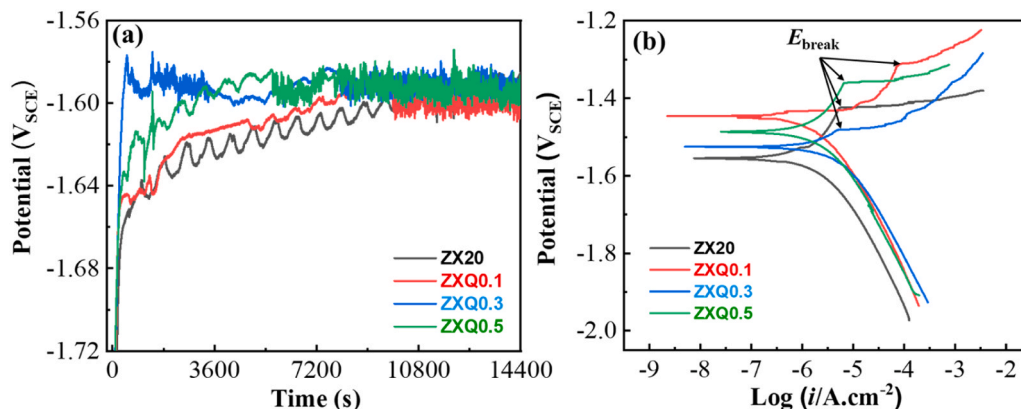


Fig. 14. (a) Open circuit potential evolution and (b) potentiodynamic polarization curves of the as-extruded alloys immersed in Hanks' solution at $37 \pm 1^\circ \text{C}$ for 12 h.

alloy exhibit positive phase angles at lower frequencies ($<0.04 \text{ Hz}$), in response to the inductive behavior caused by the adsorption and desorption of the corrosion products from the sample surface.

The EIS data were fitted using appropriate equivalent circuit (EC) models, as shown in Fig. 15(c), which were proposed based on the observed corrosion morphologies and designed to reflect the graphical features of the EIS diagrams. In the proposed circuits, R_s represents the

resistance of the Hanks' solution. Two Randles-type elements (a parallel connection of a resistor and a constant phase element, CPE) were used to model the superimposed capacitive behaviors, with the CPE accounting for surface heterogeneity [37]. R_{ct} and CPE_{dl} correspond to the charge transfer resistance and the non-ideal capacitive behavior of the electrical double layer [37,38], respectively. R_f and CPE_f represent the resistance and capacitance of the corrosion product film formed on the sample

Table 5

Tafel extrapolation results of the studied PDP curves.

Alloys	E_{corr} (V vs SCE)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_c (mV/decade)	$P_i(\times 10^{-2} \text{ mm/year})$
ZX20	-1.56	2.68	-225.99	6.13
ZXQ0.1	-1.45	2.10	-218.40	4.80
ZXQ0.3	-1.53	5.93	-228.23	13.5
ZXQ0.5	-1.49	3.51	-247.76	8.03

surface. A series connection of a resistor R and an inductor L was used to simulate the inductance response associated with the adsorption/desorption of corrosion products on the surface.

Using the proposed ECs, the experimentally recorded EIS diagrams were adequately fitted, and the fitting results are also included, as solid lines, in Fig. 15(a,b). The fitting parameters are summarized in Table 6, the goodness of the fit was verified by the reduced χ^2 value. It is evident that the fitted values of R_{ct} and CPE_{dl} are strongly influenced by the Ag content of the samples, indicating that the impedance associated with charge transfer across the double layer is Ag-dependent. The ZX20 alloy possesses a R_{ct} value of $2103 \Omega \cdot \text{cm}^2$, which is dramatically higher than that of the Ag-containing alloys. The R_{ct} values indirectly represent the intrinsic corrosion resistance of the samples, thereby suggesting that Ag addition negatively impacts corrosion performance. However, higher R_{ct} values alone do not necessarily indicate better corrosion resistance, as corrosion propagation is also influenced by the corrosion product film that accumulates on the sample surface. In the present study, the ZXQ0.1 alloy exhibits the highest R_f value, possibly due to its compromised intrinsic corrosion resistance—as indicated by its lowest R_{ct} —which may have led to the formation of a thicker corrosion product layer on the sample surface, thereby hindering the mass transfer process. A comparison of R_f and R_{ct} values across the samples suggests that the accumulation of corrosion products on the surface contributes more significantly to the overall corrosion resistance.

Based on the experimental evidence provided in the present study, the corrosion mechanism of Mg-Zn-Ca-Ag alloys in the Hanks' solution is

proposed and schematically illustrated in Fig. 16. Once upon immersion in the solution, a rather thin passive film rapidly formed on the sample surface due to the high reactivity of Mg (as confirmed by the rapid rise of OCP values shown in Fig. 14(a)). However, such passive film is not able to provide any sustained protection because of its low BPR value. The corrosive medium readily penetrates through the passive film to contact with the substrate that contains considerable amount of secondary phase particles. Our previous work had demonstrated that the secondary phase particles possess an electrode potential significantly different with that of the α -Mg matrix, readily initiate galvanic corrosion that propagate both laterally and vertically. In the process, the α -Mg matrix is dissolved, releasing Mg^{2+} ions into the electrolyte. The Mg^{2+} combines with the surrounding OH^- in the electrolyte to deposit $\text{Mg}(\text{OH})_2$ in the corrosion sites (Fig. 16(b)). Further, the Hanks' solution contains high concentration of Ca^{2+} (1.26 mM) and $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ (0.9 mM) ions, exceeding the solubility product (K_{sp}) of calcium phosphates. The standard K_{sp} of tricalcium phosphate at 25 °C is $2.07 \times 10^{-33} (\text{mol}^5 \cdot \text{L}^{-5})$ [39]. More rigorously, Gregory et al. [40] provided a temperature-dependent expression for $\beta\text{-Ca}_3(\text{PO}_4)_2$, from which the K_{sp} at 37 °C is estimated to be $\sim 2.8 \times 10^{-30} (\text{mol}^5 \cdot \text{L}^{-5})$, which is far lower than the ionic activity product calculated for the present immersion environment. This large supersaturation provides strong thermodynamic driving force for the spontaneous nucleation and precipitation of calcium phosphate on the alloy surface, forming a flocculent $\text{Ca}_3(\text{PO}_4)_2$ deposit on top of the $\text{Mg}(\text{OH})_2$ (Fig. 16(c)).

3.4. Dependence of tensile properties on immersion time

The premature mechanical failure compromises the loading capacity of the implants, therefore, it is evaluated in the present study, as shown in Fig. 17. It is clear that the degradation of the samples in the Hank's solution has deteriorated their mechanical integrity. Prior to immersion, all the samples possessed rather close mechanical strength, with an ultimate tensile strength (UTS) of around 250 MPa, a yielding strength (YTS) of approx. 154 MPa and an exceptional elongation to failure of around 30 %. These initial mechanical properties substantially exceed

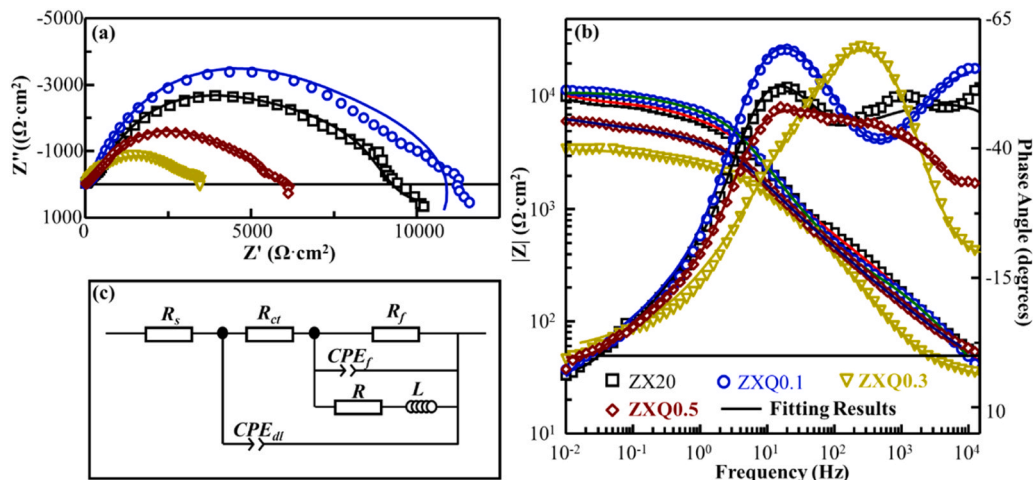


Fig. 15. The EIS diagram of the studied alloy after immersion in Hanks' solution for 12 h, (a) Nyquist plots, (b) Bode Plots, (c) Equivalent Circuit Model.

Table 6

Parameter values used for fitting the EIS diagram shown in Fig. 15.

Alloys	R_s $/\Omega \cdot \text{cm}^2$	R_{ct} $/\Omega \cdot \text{cm}^2$	CPE_{dl-T} $/\mu\text{F} \cdot \text{s}^{n-1} \cdot \text{cm}^{-2}$	CPE_{dl-P}	R_f $/\Omega \cdot \text{cm}^2$	CPE_f-T $/\mu\text{F} \cdot \text{s}^{n-1} \cdot \text{cm}^{-2}$	CPE_f-P	R $/\Omega \cdot \text{cm}^2$	L $/\text{MH cm}^{-2}$	χ^2
ZX20	26.5	2103	25	0.61	7667	0.89	0.96	1	1.0	0.002
ZXQ0.1	26.5	610	15	0.65	10288	3.2	0.96	1	1.9	0.003
ZXQ0.3	26.5	1514	15	0.78	2039	160	0.45	1	0.25	0.003
ZXQ0.5	26.5	1745	37	0.61	4155	1.5	0.98	1	0.57	0.002

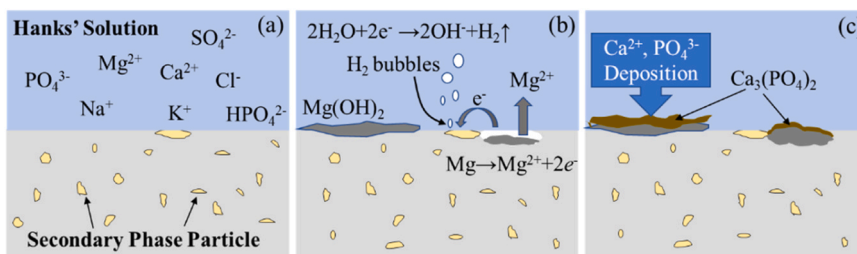


Fig. 16. Schematic illustration of reactions between magnesium alloy and Hanks' solution: (a) immersion of the sample in the solution, (b) commencement of galvanic corrosion around secondary phase particle to form $\text{Mg}(\text{OH})_2$ and H_2 , (c) the lateral propagation of the corrosion sites and spontaneous deposition of $\text{Ca}_3(\text{PO}_4)_2$ on the sample surface.

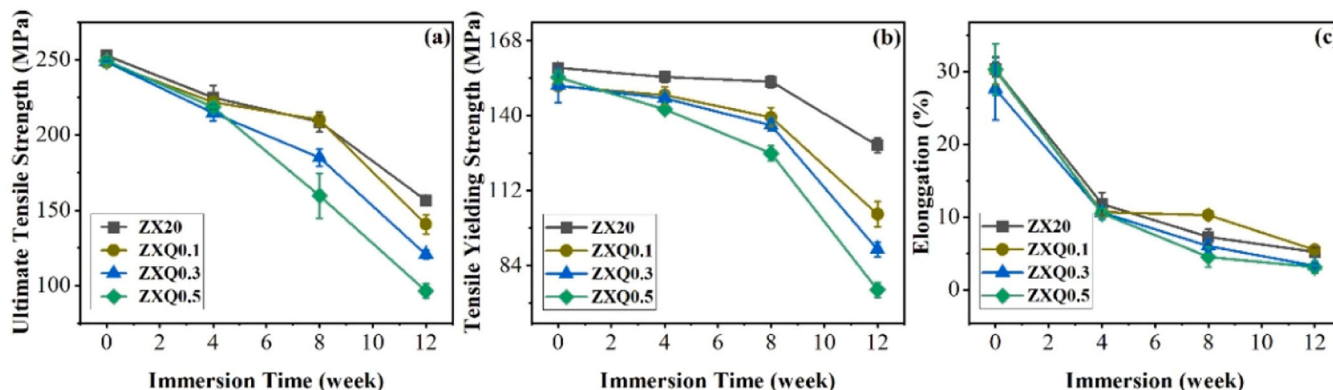


Fig. 17. Mechanical deterioration of the studied alloys with immersion time, (a) Ultimate tensile strength, (b) Tensile yielding strength and (c) Tensile elongation.

the requirements for biological loading. Nevertheless, the UTS of all the samples dramatically reduced almost linearly with increasing immersion time in the Hanks' solution. Specifically, the UTS of all the alloys dropped to around 220 MPa after 4 weeks' immersion. Following 12 weeks' immersion, the UTS decreased to 156.5 ± 0.7 MPa, 140.7 ± 6.4 MPa, 120.7 ± 2.8 MPa, and 96.5 ± 4.5 MPa for the ZX20, ZXQ0.1, ZXQ0.3 and ZXQ0.5 alloy, respectively (Fig. 17(a)). The YTS of the samples reduced with the immersion time, but followed different trajectories. During the first 8 weeks' immersion, the YTS of the alloys with Ag content of ≤ 0.3 wt% decreased only marginally. In contrast, the ZXQ0.5 alloy exhibited a substantial drop to 126.0 ± 2.8 MPa. Further extending the immersion time to 12 weeks led to dramatic YTS decrease for all the samples (Fig. 17(b)). The elongation of all samples degraded rapidly from $\sim 30\%$ to $\sim 10\%$ during the first four weeks of immersion. Subsequently, the degradation rate slowed. After further immersion, the ZX20 and ZXQ0.1 alloys maintained an elongation of approximately 5.0 %, whereas the ZXQ0.3 and ZXQ0.5 alloys fractured at a much lower elongation of around 3.0 % (Fig. 17(c)).

The addition of Ag to the ZX20 alloy did not significantly alter its microstructure (as confirmed in Section 3.1); consequently, all samples exhibited similar initial mechanical properties. The divergence in properties observed during immersion is therefore primarily attributed to differences in corrosion behavior. Corrosion testing confirmed that the ZXQ0.5 alloy experienced the most severe degradation (Fig. 5), resulting in its inferior mechanical performance. During tensile testing, stress concentrated at the tips of the resulting corrosion pits, promoting the nucleation and propagation of cracks. Elongation is considerably more sensitive to such surface defects than strength, which explains its more rapid decline initially. Despite this degradation, all samples retained a mechanical strength superior to that of natural bone [41] after 12 weeks of immersion, confirming their mechanical suitability for biomedical implants.

Prolonged immersion in Hank's solution leads to the formation of corrosion pits and locally thinned regions that serve as strong stress

concentrators, facilitating premature crack initiation and accelerating tensile failure. The peripheral corrosion layer formed during immersion is porous and mechanically fragile; its progressive thickening further reduces the effective load-bearing cross-section, thereby accounting for the observed decline in tensile properties.

The tensile-fractured after 4 and 12 weeks of immersion (Fig. 18) corroborate this mechanism. The fracture surfaces exhibit a pronounced stratified structure characterized by a thickened lamellar corrosion layer with loose consolidation and numerous corrosion-induced microcracks, indicating that failure is dominated by corrosion-assisted crack nucleation rather than the intrinsic plasticity of the alloy. Quantitative measurements show that the uncorroded fracture-area fractions after 12 weeks were 52.2 % (ZX20), 54.9 % (ZXQ0.1), 22.0 % (ZXQ0.3), and 12.9 % (ZXQ0.5), consistent with the trend in residual UTS. Furthermore, alloys with higher Ag contents (ZXQ0.3 and ZXQ0.5) exhibited severe material loss ($>75\%$ cross-section degradation), suggesting that although Ag addition may enhance antibacterial properties, excessive Ag significantly compromises corrosion resistance and mechanical retention. In contrast, ZX20 and ZXQ0.1 preserved more than half of their uncorroded cross-section, demonstrating a more favorable balance between corrosion behavior and mechanical integrity.

4. Conclusions

This study extensively explores the effect of Ag addition on the degradation of the Mg-2Zn-0.2Ca alloys in the Hanks' solution. The major conclusions from the study are as follows:

(1) The addition of Ag promoted dynamic recrystallization in the as-extruded Mg-2Zn-0.2Ca alloys and refined the secondary phases, while the overall microstructure remained largely unchanged. However, grain coarsening was observed with Ag addition, with the average grain size increasing from $6.6 \pm 2.7 \mu\text{m}$ to $8.2 \pm 3.8 \mu\text{m}$.

(2) The degradation behavior of Mg-2Zn-0.2Ca alloys was apparently affected by Ag content. The alloy containing 0.1 wt% Ag and 0.5 wt% Ag

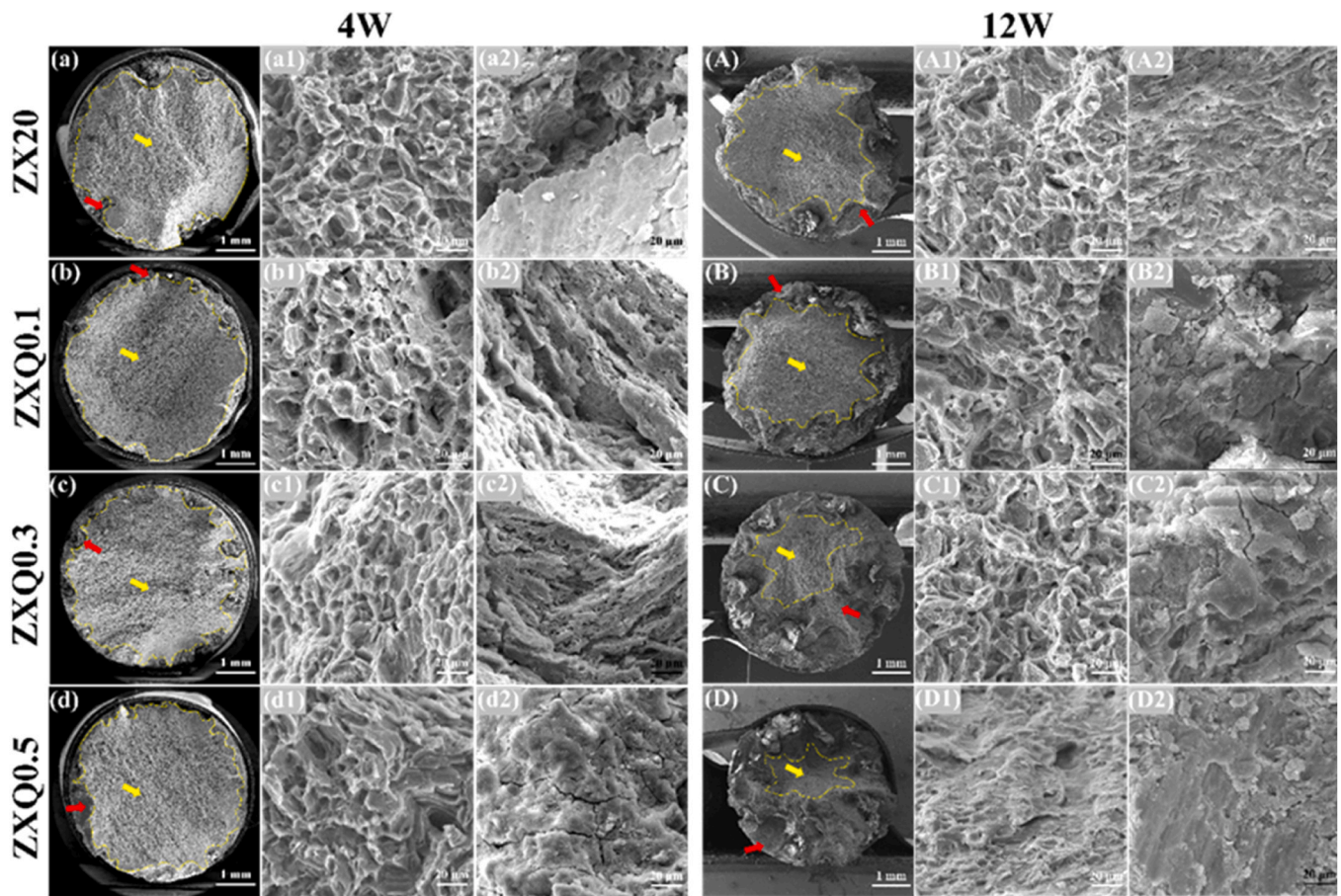


Fig. 18. SEM images of the tensile-fractured surfaces of the studied alloys after immersion in Hank's solution for 4 and 12 weeks: (a1, A1, b1, B1, c1, C1, d1, D1) shows the enlarged image at the yellow arrow, and (a2, A2, b2, B2, c2, C2, d2, D2) shows the enlarged image at the red arrow.

exhibited the minimum and maximum corrosion rate of 0.10 ± 0.03 mm/y and 0.22 ± 0.02 mm/y, respectively. Nevertheless, all the alloys exhibited degradation rate significantly lower than that applicable for biomedical applications.

(3) In Hanks' solution, the corrosion products formed on Mg-2Zn-0.2Ca-xAg alloy surfaces exhibited a bilayer structure, consisting of an inner layer of $\text{Mg}(\text{OH})_2$ and an outer layer predominantly composed of calcium phosphates $\text{Ca}_3(\text{PO}_4)_2$. The deposition of $\text{Ca}_3(\text{PO}_4)_2$ may enhance the surface bioactivity of the developed alloys.

(4) Despite the reduction of mechanical properties with immersion, all samples retained sufficient strength for biological application where load-bearing capacity is of concern. The ZXQ0.1 alloy presented a UTS, YTS and elongation of 140.7 ± 6.8 MPa, 103.3 ± 4.7 MPa, and 5.5 ± 0.6 %, respectively.

CRediT authorship contribution statement

Gang Zeng: Resources, Investigation. **Yi Chen:** Investigation, Data curation. **Chuming Liu:** Validation, Resources, Project administration. **Yonghao Gao:** Writing – review & editing, Validation, Funding acquisition. **Fang Yi:** Writing – original draft, Investigation. **Chao Cao:** Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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