

Article

Optimization of Hopeite Coating Formation on AZ91D Magnesium Alloy by Chemical Conversion: The Role of Treatment Time

Xian Zhang ^{1,*}, Hong-Hong Zhang ¹, Kang Wu ¹, Zhi-Bin Li ², Zhong-Nan Gao ², Quan-Hai Guo ² and Hao-Cun Wang ²

¹ College of Chemical Engineering and Materials, Shandong University of Aeronautics, Binzhou 256600, China

² Weifang Fengdong Heat Treating Co., Ltd., Weifang 261500, China

* Correspondence: zhangxiantaian@163.com

Highlights

- Three-in-one conversion and galvanic coupling processes were adopted for coating formation.
- The influence of treatment time on hopeite coating formation was discussed.
- The uniform and fine hopeite coating was fabricated on AZ91D Mg alloy at 55 °C for 15 min.

Abstract

Hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) coatings, obtained via zinc phosphate chemical conversion (ZPCC), have gained increasing attention in the biomedical field. Such coatings are particularly appealing owing to their combined capability of excellent corrosion resistance and biocompatibility. This study investigates the influence of processing time on the formation of hopeite coatings on AZ91D magnesium alloy by zinc phosphate chemical conversion (ZPCC). X-ray diffraction (XRD) analysis confirmed that the coatings primarily consisted of hopeite, with trace amounts of phosphophyllite. The maximum coating mass and thickness were achieved after a 30 min treatment at 55 °C. Electrochemical measurements demonstrated superior corrosion resistance for coatings formed within 15–30 min. Additionally, coating self-adhesion tests revealed strong bonding between the coating and the substrate.

Keywords: AZ91D Mg alloy; hopeite; corrosion resistance; phosphate chemical conversion

Academic Editor: Charafeddine

Jama

Received: 30 May 2026

Revised: 22 June 2026

Accepted: 24 June 2026

Published: 26 June 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Phosphate chemical conversion (PCC) technology is widely recognized as a critical surface pretreatment method for metallic substrates, primarily employed to enhance corrosion resistance, wear resistance, and interfacial adhesion of underlying materials [1,2]. Its industrial prominence stems from three key advantages: rapid coating formation kinetics, compatibility with complex geometries, and cost-effectiveness [3,4]. PCC solutions are systematically categorized based on their predominant metal ions, including zinc, manganese, iron, zinc–calcium, magnesium, and chromate systems [5–8]. Among these,

zinc phosphate chemical conversion (ZPCC) has emerged as the most industrially prevalent variant due to its superior corrosion protection performance. This method is highly versatile and can be applied to a range of substrates including mild steels, galvanized steels, stainless/nitrided steels, magnesium alloys, titanium, and aluminum [3,9,10]. Various fabrication techniques, such as chemical treatment, electrochemical deposition, and hydrothermal synthesis, have been successfully employed to produce ZPCC coatings [5,11].

The hopeite phase ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$), constituting the primary component of ZPCC coatings, finds extensive applications in electric motors, automotive components, and corrosion-resistant pigments [12,13]. Beyond conventional industrial uses, hopeite exhibits significant biomedical potential, particularly as a surface modification for zinc phosphate dental cements, owing to its exceptional osteogenic properties and biocompatibility [12,14]. In vitro studies have demonstrated excellent attachment and proliferation of both osteogenic cells and human fibroblasts on titanium substrates modified with hopeite coatings [15,16]. Building upon these findings, our previous work successfully deposited hydroxyapatite (HA) coatings onto hopeite-modified surfaces via simulated body fluid (SBF) immersion, further extending the functional potential of such interfaces [17].

Magnesium (Mg) and its alloys are important lightweight structural materials, widely used in various industries due to their low density, good machinability, and biocompatibility [8,18]. To overcome this drawback, extensive research has focused on surface modification techniques aimed at improving both the corrosion resistance and biocompatibility of Mg-based materials. Numerous surface treatment approaches have been investigated to address this challenge, including sol-gel [19–21], chemical conversion process [22,23], plasma electrolytic oxidation [24,25], electrodeposition [26], and physical vapor deposition (PVD) [27]. Among these, chemical conversion coatings are considered particularly promising because of their cost-effectiveness, scalability, and proven corrosion protection performance [28–30]. Notably, ZPCC has gained recognition as an effective pretreatment for Mg alloys, offering both corrosion protection and improved adhesion for subsequent painting processes. Despite these advancements, the potential application of ZPCC for biomedical Mg alloys remains insufficiently explored.

In this study, hopeite coatings were fabricated on AZ91D Mg alloys via a conventional chemical conversion method using a medium-temperature phosphating solution combined with a galvanic coupling process. The effect of processing time on the characteristics of the coatings was systematically investigated. The primary objective was to determine the optimal processing time for the formation of uniform hopeite coatings.

2. Materials and Methods

Commercially available AZ91D Mg alloy substrates (Dongguan Hongdi Metal Materials Co., Ltd., Dongguan, China), having the composition (wt.%) Al: 8.3%–9.7%, Zn: 0.35%–1.0%, Mn: 0.15%–0.5% and Mg: balance, were utilized for this study. The specimens were abraded using 240-grit emery paper, followed by rinsing with distilled water. Afterwards, the samples were immersed in a chemical conversion solution bath at 55 °C for different duration times from 5 to 30 min at a pH value of 2.75. The flow chart and the composition of the chemical conversion solution for preparing ZPCC are given in Figure 1. Zinc oxide, phosphoric acid, nitric acid, and calcium nitrate tetrahydrate were used as the primary reagents. All chemicals were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

The ZPCC bath, formulated to produce a biocompatible and osteogenic hopeite phase, was maintained at a pH of 2.75 and a temperature of 55 °C. These conditions were chosen to balance substrate dissolution with coating nucleation while ensuring sufficient reaction kinetics. The systematic optimization of bath composition, pH, and temperature

will be reported separately. To accelerate film formation, Mg-Fe coupling was adopted, following the approach described in a previous work [8]. Preliminary experiments showed that treatment beyond 30 min resulted in bath precipitation and coating defects; therefore, 30 min was selected as the endpoint in this study.

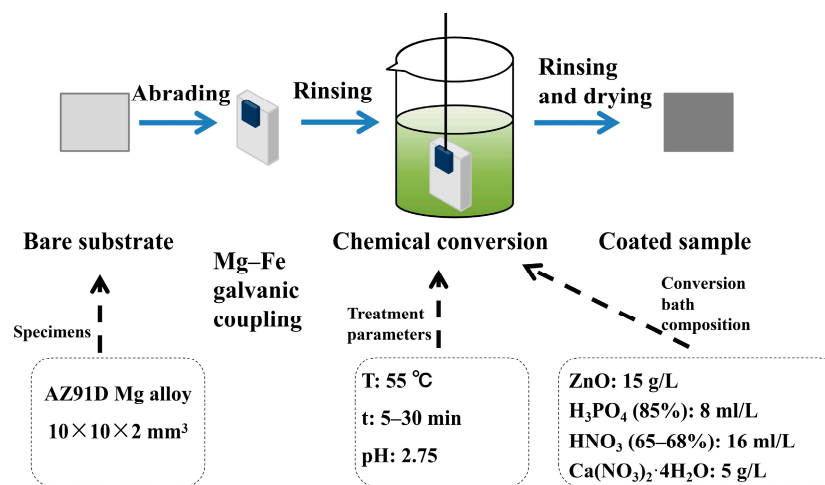


Figure 1. Schematic illustration of the fabrication of ZPCC coating.

Coating mass and thickness measurements were conducted according to a previously established method [5,11], with all reported values representing the mean of five replicate determinations. The sample weights were measured using a high-precision analytical balance (± 0.1 mg).

The coating mass (M , $\text{g}\cdot\text{m}^{-2}$) was calculated as follows (Equation (1)):

$$M = \frac{m_1 - m_2}{A} \quad (1)$$

where m_1 and m_2 denote the sample weights (g) before and after coating removal, respectively, and A represents the substrate area (m^2). The stripping process, defined as the removal of the coating, was carried out at 70 °C for 5 min in a solution composed of 100 g/L NaOH, 4 g/L $\text{C}_6\text{H}_{15}\text{NO}_3$, and 90 g/L $\text{C}_6\text{H}_{10}\text{N}_2\text{Na}_4\text{O}_4$ [5,31]. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The coating thickness was measured using an eddy current thickness gauge (CT-100, Quzhou Aipu Measuring Instruments Co., Ltd., Quzhou, China).

To evaluate the self-adhesion strength of the coatings, an ultrasonic weight loss method was employed. The variation in mass before and after ultrasonic cleaning (KQ-500VDE, KunShan Ultrasonic Instruments Co., Ltd., Kunshan, China) served as an indicator of adhesion strength. For each experimental group, four randomly selected samples were initially weighed after chemical conversion treatment (denoted as m_1). Subsequently, the samples were subjected to ultrasonic cleaning in anhydrous ethanol for varying times. After drying, their mass was re-measured (denoted as m_t , where t represents ultrasonic duration, ranging from 5 to 900 s). The calculation formula of the coating self-adhesion strength is as follows:

$$W_t = \frac{m_1 - m_t}{A} \quad (2)$$

where W_t ($\text{g}\cdot\text{m}^{-2}$) represents the coating mass, m_1 and m_t (g) denote the sample weights before and after ultrasonic cleaning in anhydrous ethanol, respectively, and A (m^2) represents the substrate area.

The microstructures of the coatings were studied using an SNE-Alpha ultra-high-resolution desktop scanning electron microscope (SEC Co., Ltd., Suwon, Gyeonggi-do, South Korea). The phase composition of the coatings was characterized through X-ray

diffraction (XRD) using a Rigaku D/max- γ B diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu K α radiation, which was operated at 40 kV and 100 mA. The diffraction patterns were recorded in the 2θ range of 5–80° with a scanning rate of 8°/min. The surface morphology of the coating was examined using a super-depth-of-field microscope (DVM6A, Leica, Wetzlar, Germany).

Electrochemical measurements were performed to evaluate corrosion resistance using a standard three-electrode system, comprising a platinum counter electrode, a saturated calomel reference electrode (SCE), and the sample (either uncoated or coated) as the working electrode with a 1 cm² exposed area. All electrochemical tests were conducted in a 0.9 wt.% NaCl solution (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). A CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China) was used for the measurements. The potentiodynamic polarization curves were recorded at a constant scan rate of 1 mV/s.

3. Results and Discussion

3.1. Coating Mass and Thickness

Figure 2 illustrates the correlation between the time interval, coating mass, and thickness of ZPCC coatings deposited at 55 °C. It is clearly observed that both the coating mass and thickness rise with the increase in reaction time. The coating mass increased from 41.63 ± 9.53 to 109.01 ± 15.7 g/m² as the deposition time extended from 5 to 30 min, whereas the coating thickness exhibited an initial rise from 76.9 ± 16.83 to 103.8 ± 28.46 μ m. Notably, both parameters followed non-linear trends, with the most pronounced variations occurring between 25 and 30 min. During this interval, the coating mass showed a gradual increase (96.47 ± 14.41 to 109.01 ± 15.7 g/m²), while the thickness decreased markedly (113.7 ± 18.68 to 103.8 ± 28.46 μ m).

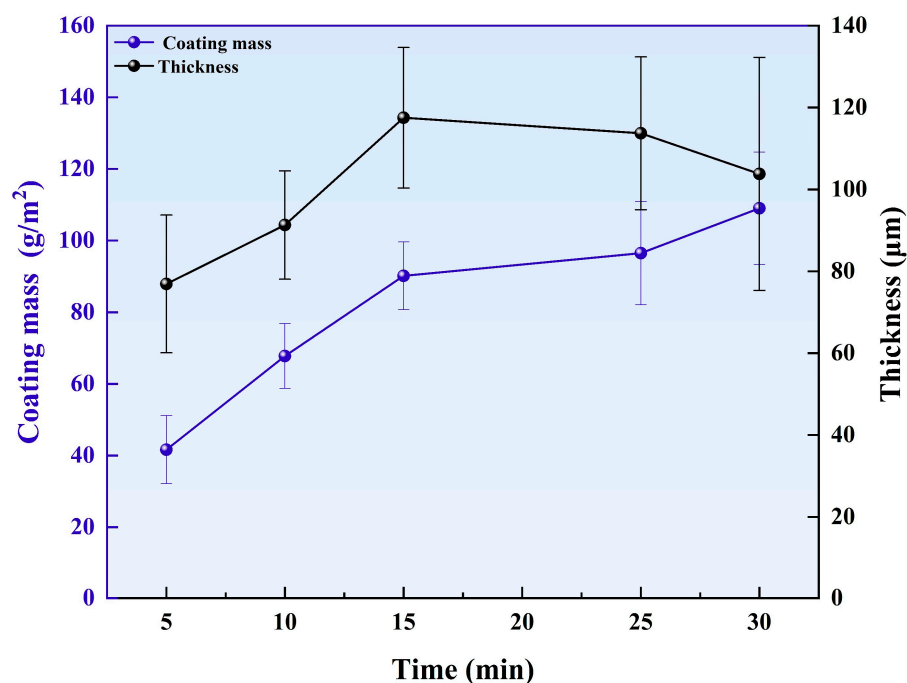


Figure 2. The coating mass and coating thickness of the ZPCC coating vs. time curves at 55 °C.

The conversion process begins with the dissolution of the oxide film, followed by nucleation and grain growth. These mechanisms drive a near-linear increase in coating mass within the first 15 min. Beyond 15 min, further coating development is governed by crystal growth, structural reorganization, and secondary crystallization [5]. However, as

the system approaches saturation, the rate of coating formation balances with partial crystal dissolution, resulting in negligible net coating mass change [5,23]. Coating thickness exhibits a time-dependent increase, correlating directly with processing duration. Coating mass serves as a critical quality control parameter in industrial applications, directly influencing coating uniformity [5]. During the 25–30 min, the coating mass exhibited a gradual increasing trend (from 96.45 ± 14.41 g/m² to 109.01 ± 15.7 g/m²), while the thickness demonstrated a slight reduction (from 113.7 ± 18.68 µm to 103.8 ± 28.46 µm). This apparent discrepancy, a decrease in thickness despite an increase in coating mass, can be explained by a dissolution–reprecipitation mechanism. Specifically, the reprecipitation of hopeite fills internal voids and densifies the coating structure. This densification leads to an increase in coating mass while simultaneously reducing surface roughness and overall thickness. In addition, substrate roughness may also affect coating thickness. In this study, the substrate was prepared using 240-grit emery paper, which results in a relatively high surface roughness compared to finer polishing steps. This could partially account for the observed variation in coating thickness. Future studies should adopt standardized surface preparation protocols and include quantitative roughness measurements to better elucidate the relationship between substrate condition and coating properties.

3.2. Phase Composition

The XRD patterns of ZPCC coatings treated at 55 °C for varying durations are presented in Figure 3. The diffraction analysis reveals that the coatings are primarily composed of hopeite (Joint Committee on Powder Diffraction Standards, JCPDS #37-0456), with trace amounts of phosphophyllite (JCPDS #29-1427). The formation of ZPCC coatings on the substrate occurs through the following reactions:

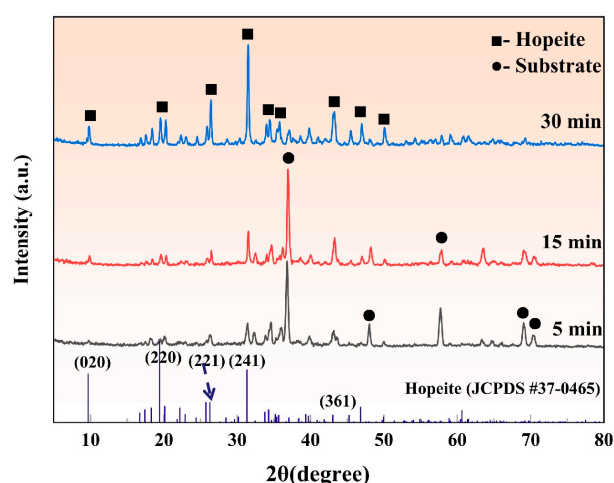
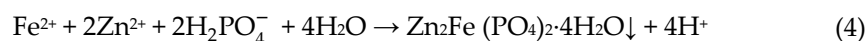
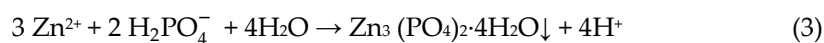


Figure 3. XRD patterns of the samples ZPCC treated for different times at 55 °C.

All coatings fabricated under varying deposition durations exhibit nearly identical XRD patterns, differing primarily in relative peak intensities (Figure 3). The sharp diffraction peaks suggest high crystallinity in all samples. Notably, the peak intensities show a progressive enhancement with prolonged processing time, demonstrating the continuous growth of the crystalline coating.

As shown in Figure 3, the diffraction intensities of the (221) and (241) planes, located at 26.3° and 31.3°, respectively, show a clear progressive enhancement with increasing

duration of ZPCC treatment. The peak intensities of both planes increase continuously with processing time from 5 to 30 min, demonstrating that the crystallographic evolution directly governs the final coating properties. Notably, the (241) plane demonstrates the most significant enhancement in diffraction intensity in (Figure 3), suggesting a preferred orientation of hopeite crystals along the (241) plane.

Hopeite is regarded as a promising multifunctional biomedical material owing to its excellent biocompatibility and its ability to transform into hydroxyapatite (HA) in a Ca^{2+} -saturated alkaline environment such as simulated body fluid (SBF) [17]. As a result, considerable research has focused on synthesizing hopeite coatings through chemical conversion methods [10,17]. In contrast, phosphophyllite, which forms at the substrate–coating interface, exhibits superior corrosion resistance in NaCl solutions and other aqueous environments owing to its higher chemical stability [10].

3.3. Microstructure Characterization

The SEM images of the coatings obtained at 55 °C under different duration times are shown in Figure 4. A continuous and uniform coating is observed across the substrate, displaying a clustered morphology consisting of granular grains. As the processing time increased, the crystal structure evolved into a more uniform and bigger morphology, suggesting the occurrence of renewed crystal nucleation and growth (Figure 4a,b) [19]. With the duration time increasing from 15 to 30 min (Figure 4b–d), both crystal growth and secondary crystallization contribute to the observed increase in coating mass and thickness (Figure 2) [10]. Notably, the coating formed after 30 min exhibits larger crystal sizes (Φ 10–40 μm) compared to those obtained at shorter durations (15–25 min) (Figure 4b,c). This increase in crystal dimensions corresponds to the higher coating mass measured at 30 min relative to samples processed for 5–25 min (Figure 2).

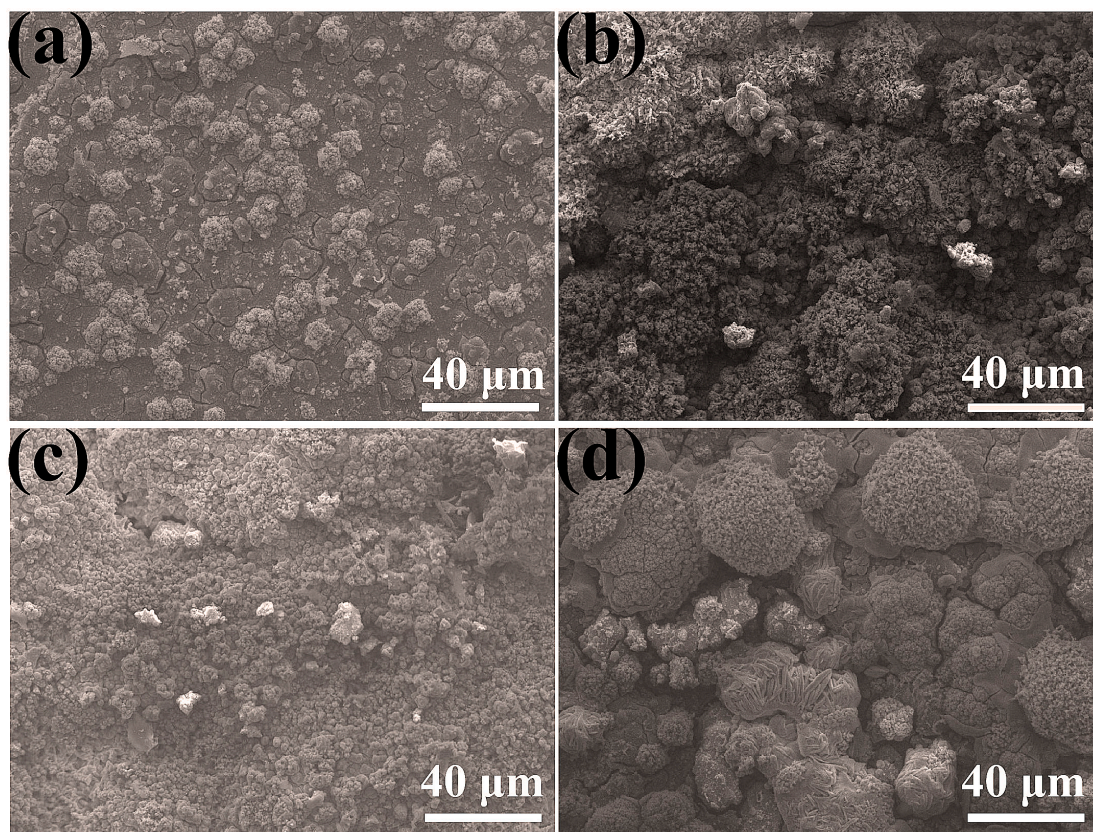


Figure 4. SEM images of the ZPCC coatings treated for different times at 55 °C: (a) 5 min, (b) 15 min, (c) 25 min, (d) 30 min.

Figure 5 presents the three-dimensional surface topography of the ZPCC coatings deposited at 55 °C for different duration times. The surfaces exhibit an irregular peak–valley morphology, which originates from the disordered arrangement of crystals and is consistent with the SEM observations in Figure 4. Among these, the coating obtained after 15 min (Figure 5a) shows a relatively uniform surface with lower roughness compared to those deposited for 25 min (Figure 5b) and 30 min (Figure 5c). In contrast, the 30 min coating demonstrates a broader distribution of feature sizes and a more pronounced disorder in its microstructure.

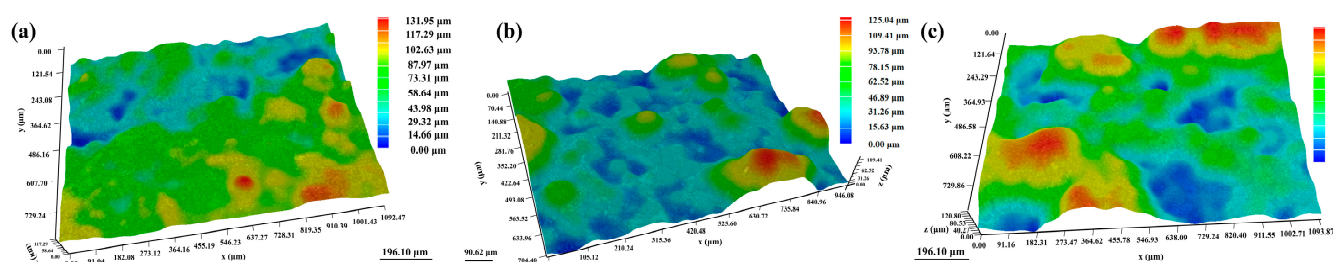


Figure 5. The 3D morphology of the hopeite coatings for different times at 55 °C: (a) 15 min, (b) 25 min, (c) 30 min.

3.4. Self-Adhesive Strength

The interfacial bonding strength between the coating layers is a critical parameter for evaluating the interlayer adhesion performance. To assess the structural integrity and adhesion properties of the conversion coating, ultrasonic cleaning was employed as an indirect characterization method. This approach leverages the pronounced dispersing and peeling effects of ultrasound, with gravimetric measurements providing quantitative evaluation of coating stability.

Figure 6 illustrates the weight loss versus ultrasonic treatment time for conversion coatings prepared at 55 °C with different duration times. As observed, the weight loss of all coatings increased non-linearly with prolonged ultrasonication. During the 0–900 s test period, the majority of mass loss occurred within the initial 0–200 s, indicating a phase of rapid coating degradation. Beyond 200 s, the weight loss tended to stabilize. This plateau may result either from the complete detachment of the coating (where maximal mass loss has been attained) or from the limited ultrasonication duration being insufficient to fully remove the coating. In the latter case, the remaining coating likely possesses strong internal cohesion and excellent adhesion to the substrate.

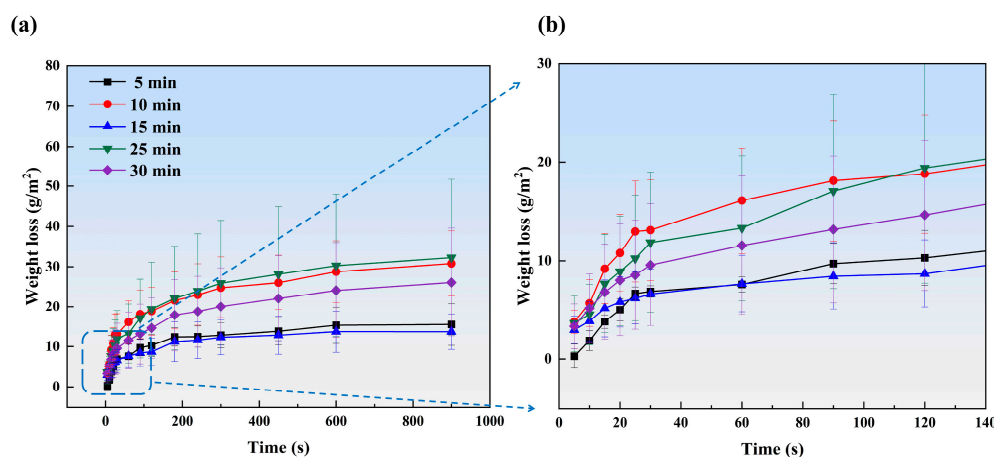


Figure 6. Curves of weight loss of coatings fabricated for different preparation times as a function of ultrasonic time at 55 °C. (a) overall image, (b) magnified image of the region indicated by the blue square in (a).

During the first 120 s of ultrasonic cleaning, the coatings exhibited a weight loss of approximately 8.8 to 19.4 g/cm², primarily due to the detachment of loosely bonded crystalline grains on the outermost surface. These superficial grains, being weakly adhered to the underlying layer, were especially susceptible to delamination under ultrasonic excitation. After exceeding 200 s of ultrasonic exposure, the mass loss stabilized considerably, indicating that most of the weakly attached surface grains had been removed and a more cohesive inner layer had been exposed. The significantly lower removal rate beyond this stage further reflects the strong interfacial adhesion of the remaining crystals adjacent to the substrate.

Notably, even after prolonged ultrasonic treatment (900 s), the cumulative weight loss of all conversion coatings remained significantly lower than their initial mass (Figure 2), indicating strong interfacial adhesion with the underlying substrate. Among the tested coatings, the coating prepared with 15 min demonstrated the lowest mass loss, highlighting its superior structural integrity and superior bonding performance relative to the other samples.

3.5. Electrochemical Investigation

The corrosion performance of the bare substrate and ZPCC coatings deposited for different duration times was assessed through potentiodynamic polarization in 0.9 wt.% NaCl solution (Figure 7). The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) are summarized in Table 1.

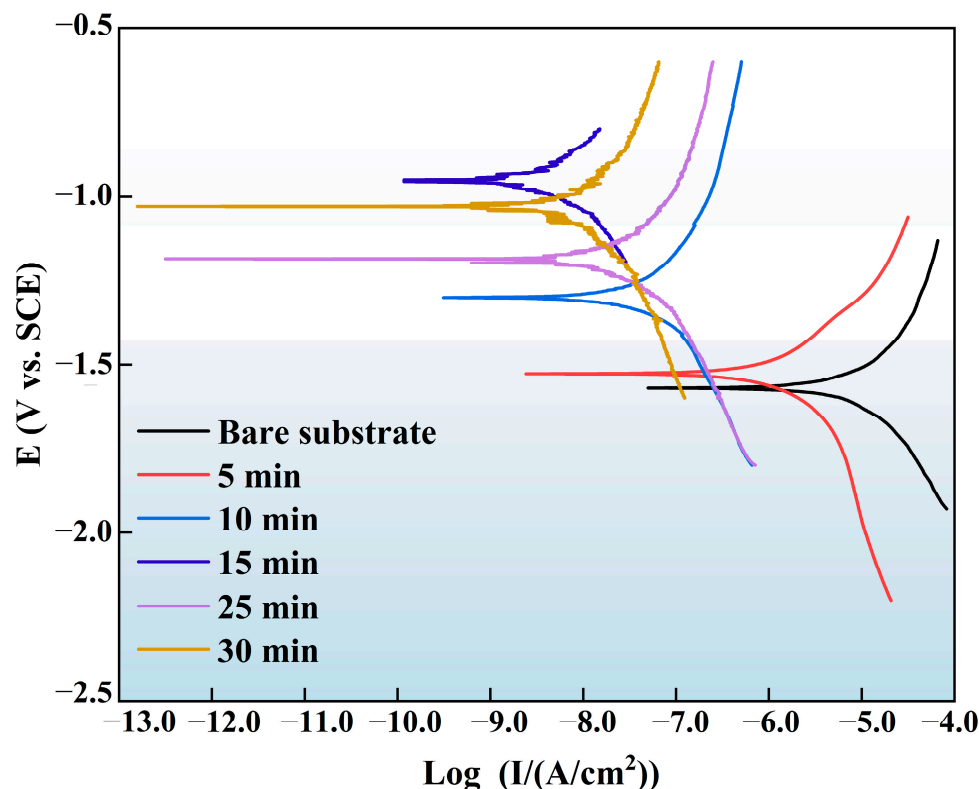


Figure 7. Potentiodynamic polarization curves of samples for different times at 55 °C and bare substrate in 0.9 wt. % sodium chloride solution.

Electrochemical polarization measurements reveal that all ZPCC-coated samples exhibit a lower I_{corr} , along with a higher E_{corr} , compared to the bare substrate (Figure 7 and Table 1). These results demonstrate the improved corrosion resistance afforded by the ZPCC coating in a 0.9 wt.% NaCl solution, which can be attributed primarily to the chemical stability of the constituent hopeite and phosphophyllite phases [10]. Notably, while the crystal morphology of the coatings remains largely unchanged regardless of treatment duration time, electrochemical evaluation reveals a clear time-dependent trend: prolonged treatment leads to a decrease in I_{corr} and a concurrent increase in E_{corr} . The improvement becomes increasingly pronounced up to 30 min, indicating that extended processing promotes superior corrosion protection. This trend is consistent with the microstructural evolution shown in Figure 4, where a denser crystalline layer and greater coating mass gain (Figure 2) collectively enhance the barrier performance of the ZPCC coating.

The enhanced performance can be attributed to microstructural evolution under prolonged treatment times. Specifically, the formation of finer and more compact crystals contributes to coating densification, which increases coating mass while leading to a slight reduction in thickness during the 25–30 min period (Figure 2). This densified structure is responsible for the improved corrosion resistance. Collectively, these morphological and physical improvements contribute to the superior barrier properties of the coatings.

Table 1. The results of potentiodynamic corrosion tests in 0.9% sodium chloride solution.

Introduction	E_{corr} (V _{SCE})	$I_{\text{corr}}, \times 10^{-6}$ (A/cm ²)
Bare	−1.58	2.140
5 min	−1.54	0.570
10 min	−1.28	0.021
15 min	−0.89	0.001
25 min	−1.17	0.010
30 min	−1.02	0.004

4. Conclusions

To systematically evaluate the influence of duration time on the formation and properties of zinc phosphate chemical conversion (ZPCC) coatings, a series of coatings was fabricated on AZ91 magnesium alloy substrates under varying treatment times. The influence of duration on key coating characteristics, including coating mass, thickness, phase composition, microstructure, and electrochemical corrosion behavior, was comprehensively investigated.

The results revealed that, while the phase composition and crystal morphology of the coatings remained consistent across different treatment durations, the coating mass, thickness, and corrosion resistance exhibited a positive correlation with prolonged duration time. Notably, coatings formed within 15–30 min demonstrated superior coating mass and enhanced corrosion resistance. Consequently, this duration range is proposed as the optimal treatment time for ZPCC coating formation under the present experimental conditions. Further studies, such as biocompatibility assessments, are currently underway to evaluate the coating's potential for biomedical applications.

Author Contributions: X.Z.: data analysis, writing, funding acquisition; H.-H.Z.: literature search, funding acquisition; K.W.: data interpretation, funding acquisition; Z.-B.L.: resources, visualization; Z.-N.G.: validation, resources; Q.-H.G. and H.-C.W.: supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Shandong Provincial Natural Science Foundation of China (ZR2021ME218, ZR2020ME018), the Shandong Provincial High-end Aluminum Manufacturing and Application Innovation and Entrepreneurship Community Project (BZGDL-XM-2025-02) and the Youth Innovation Support Program of Shandong Universities (2024KJG083).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: Authors Zhi bin Li, Zhong Nan Gao, Quan-Hai Guo and Hao-Cun Wang are affiliated with Weifang Fengdong Heat Treating Co., Ltd, and Weifang Fengdong Heat Treating Co., Ltd. provided financial support to cover the publication charges of this manuscript. The enterprise took no part in experimental design, data analysis, manuscript drafting and submission decision. All university- affiliated authors have no conflicts of interest to disclose.

References

1. Wu, Y.; Duan, Y.; Qiu, J.; Gao, X.; Ma, H. A pH-responsive intelligent coating based on composite CaCO₃ microspheres for long-term corrosion protection of Q235 carbon steel. *Appl. Surf. Sci.* **2022**, *578*, 151980. <https://doi.org/10.1016/j.apsusc.2021.151980>.
2. Li, Y.B.; Zhang, H.Q.; Lu, Y.P.; Yang, X.J.; Wang, G.D.; Wang, Y.Y.; Tang, K.L.; Huang, S.Y.; Xiao, G.Y. Construction of magnesium phosphate chemical conversion coatings with different microstructures on titanium to enhance osteogenesis and angiogenesis. *ACS Appl. Mater. Interfaces* **2024**, *16*, 21672–21688. <https://doi.org/10.1021/acsami.4c03024>.
3. Liu, B.; Zheng, Y.Z.; Xiao, G.Y.; Chen, C.Z.; Lu, Y.P. Influence of surface post-processing on crystal refinement and characteristics of hopeite coating by phosphating. *Coatings* **2021**, *11*, 541. <https://doi.org/10.3390/coatings11050541>.
4. Li, Y.B.; Lu, Y.P.; Du, C.M.; Zuo, K.Q.; Wang, Y.Y.; Tang, K.L.; Xiao, G.Y. Effect of reaction temperature on the microstructure and properties of magnesium phosphate chemical conversion coatings on titanium. *Molecules* **2023**, *28*, 4495. <https://doi.org/10.3390/molecules28114495>.
5. Narayanan, T.S.N.S. Surface pretreatment by phosphate conversion coatings—A review. *Rev. Adv. Mater. Sci.* **2005**, *9*, 130–177.
6. Jian, S.Y.; Yang, C.Y.; Chang, J.K. Robust corrosion resistance and self-healing characteristics of a novel Ce/Mn conversion coatings on EV31 magnesium alloys. *Appl. Surf. Sci.* **2020**, *510*, 145385–145399. <https://doi.org/10.1016/j.apsusc.2020.145385>.
7. Kraš, A.; Kramar, D.; Milošev, I. Experimental approach and assessment of Zr conversion coatings on al alloy using response surface methodology. *Corros. Sci.* **2025**, *249*, 112824–112838. <https://doi.org/10.1016/j.corsci.2025.112824>.
8. Zhang, X.; Xiao, G.Y.; Jiang, C.C.; Liu, B.; Li, N.B.; Zhu, R.F.; Lu, Y.P. Influence of process parameters on microstructure and corrosion properties of hopeite coating on stainless steel. *Corros. Sci.* **2015**, *94*, 428–437. <https://doi.org/10.1016/j.corsci.2015.02.021>.
9. Ren, S.; Sun, H.-B.; Meng, F.; Cui, Y.; Liu, R.; Hu, X.; Wang, F.; Liu, L. Polyoxometalate-polypyrrole synergism: A new approach to boost oxide film formation for fabricating self-passivating organic coatings. *Appl. Surf. Sci.* **2025**, *699*, 163183. <https://doi.org/10.1016/j.apsusc.2025.163183>.
10. Du, C.M.; Zuo, K.Q.; Ma, Z.L.; Zhao, M.R.; Li, Y.B.; Tian, S.; Lu, Y.P.; Xiao, G.Y. Effect of substrates performance on the microstructure and properties of phosphate chemical conversion coatings on metal surfaces. *Molecules* **2022**, *27*, 6434–6450. <https://doi.org/10.3390/molecules27196434>.
11. Zhang, X.; Xiao, G.Y.; Jiao, Y.; Zhao, X.C.; Lu, Y.P. Facile preparation of hopeite coating on stainless steel by chemical conversion method. *Surf. Coat. Technol.* **2014**, *240*, 361–364. <https://doi.org/10.1016/j.surfcoat.2013.12.054>.
12. Sadeghi-Aghbash, M.; Rahimnejad, M. Zinc phosphate nanoparticles: A review on physical, chemical, and biological synthesis and their applications. *Curr. Pharm. Biotechnol.* **2022**, *23*, 1228–1244. <https://doi.org/10.2174/1389201022666211015115753>.
13. Školáková, A.; Pinc, J.; Jablonská, E.; Školáková, T.; Veřtát, P.; Janebová, B.; Kutová, A.; Čapek, J.; Hosová, K.; Vojtěch, D.; et al. A zinc phosphate layered biodegradable Zn-0.8Mg-0.2Sr alloy: Characterization and mechanism of hopeite formation. *Surf. Coat. Technol.* **2024**, *487*, 130986. <https://doi.org/10.1016/j.surfcoat.2024.130986>.
14. Zuo, K.Q.; Xiao, G.Y.; Du, C.M.; Liu, B.; Li, Y.B.; Lu, Y.P. Controllable phases evolution and properties of zinc-phosphate/strontium-zinc-phosphate composite conversion coatings on Ti: Effect of temperature. *Surf. Coat. Technol.* **2022**, *447*, 128885. <https://doi.org/10.1016/j.surfcoat.2022.128885>.

15. Zhao, X.C.; Xiao, G.Y.; Zhang, X.; Wang, H.Y.; Lu, Y.P. Ultrasonic induced rapid formation and crystal refinement of chemical converted hopeite coating on titanium. *J. Phys. Chem. C* **2014**, *111*, 1910–1918. <https://doi.org/10.1021/jp408444j>.
16. Zuo, K.; Li, A.; Si, T.; Lei, W.; Liu, Y.; Zhang, L.; Zhang, T.; Xiao, G.; Lu, Y.; Li, N. Structural optimization of Sr/Zn-phosphate conversion coatings triggered by ions preloading on micro/nanostructured titanium surfaces for bacterial infection control and enhanced osteogenesis. *J. Nanobiotechnology* **2025**, *23*, 361. <https://doi.org/10.1186/s12951-025-03443-6>.
17. Zhang, X.; Xiao, G.Y.; Liu, B.; Jiang, C.C.; Li, N.B.; Lu, Y.P. The formation of hydroxyapatite layer onto hopeite coating on stainless steel substrate. *Corros. Sci.* **2016**, *111*, 216–229. <https://doi.org/10.1016/j.corsci.2016.05.012>.
18. Hsiao, T.H.; Lin, C.S. Mn oxide conversion coating on AZ31B Mg alloy with hexafluorozirconate as an inhibitor in the permanganate conversion bath. *Appl. Surf. Sci.* **2024**, *660*, 159960. <https://doi.org/10.1016/j.apsusc.2024.159960>.
19. Wang, Y.; Xiao, W.; Blawert, C.; Serdechnova, M.; Feng, L.; Wang, J.; Pan, F. Conception of corrosion converter for magnesium alloy surface: Replacing the corrosion product layer with a protective coating in high concentration corrosion medium. *Corros. Sci.* **2025**, *244*, 112639. <https://doi.org/10.1016/j.corsci.2024.112639>.
20. Galvan-Reyes, C.; Salinas-Rodríguez, A.; Fuentes-Aceituno, J. Degradation and crystalline reorganization of hureaulite crystals during the manganese phosphating of a high strength steel. *Surf. Coat. Technol.* **2015**, *275*, e10–e20. <https://doi.org/10.1016/j.surf-coat.2015.05.030>.
21. Zengin, H.; Hassel, A.W. Magnesium alloys with rare earth elements—A review of the recent progress on the corrosion properties. *Corros. Sci.* **2025**, *249*, 112827.
22. Merino, E.; Durán, A.; Castro, Y. The Role of Silane Sol-Gel Coatings on the Corrosion Protection of Magnesium Alloys. In *Current Trends in Magnesium (Mg) Research*; Sunkari, S.S.S., Ed.; IntechOpen: London, UK, 2022. <https://doi.org/10.5772/intechopen.102085>.
23. Yang, X.; Lu, X.; Zhou, Y.; Xie, Y.; Yang, J.; Wang, F. Formation of protective conversion coating on Mg surface by inorganic inhibitor. *Corros. Sci.* **2023**, *215*, 111044–111056. <https://doi.org/10.1016/j.corsci.2023.111044>.
24. Wang, S.; Liu, X.; Wang, L.; Wen, Q.; Du, N.; Huang, J. Formation mechanism and properties of fluoride–phosphate conversion coating on titanium alloy. *RSC Adv.* **2017**, *7*, 16078–16086. <https://doi.org/10.1039/C6RA27199E>.
25. Yang, C.; Chen, P.; Wu, W.; Sheng, L.; Zheng, Y.; Chu, P.K. A review of corrosion-resistant PEO coating on Mg alloy. *Coatings* **2024**, *14*, 451. <https://doi.org/10.3390/coatings14040451>.
26. Ramu, A.; Yang, D.; Song, M.; Choi, D. Advancements in integrating mofs into micro-arc oxidation coatings on mg alloys: A perspective on peo-mof coatings as innovative corrosion inhibitors. *J. Magnes. Alloys* **2024**, *12*, 4363–4394. <https://doi.org/10.1016/j.jma.2024.11.029>.
27. Akbarzadeh, F.Z.; Rajabi, M.; Jamaati, R.; Braem, A. Microstructural tuning of AZ91 magnesium alloy for improved morphology and corrosion protection of electrodeposited hydroxyapatite coatings. *Corros. Sci.* **2025**, *245*, 112678–112682. <https://doi.org/10.1016/j.corsci.2025.112678>.
28. Song, Q.; Yang, L.; Yi, F.; Chen, C.; Guo, J.; Qi, Z.; Song, Y. Antibacterial pure magnesium and magnesium alloys for biomedical materials—A review. *Crystals* **2024**, *14*, 939. <https://doi.org/10.3390/cryst14110939>.
29. Chen, C.W.; Aktug, S.L.; Chang, C.J.; Lee, Y.L.; Ger, M.D.; Jian, S.Y. A chromate-free and convenient route to fabricate thin and compact conversion coating for corrosion protection on LZ91 magnesium alloy. *Nanomaterials* **2022**, *12*, 1614. <https://doi.org/10.3390/nano12091614>.
30. Salman, S.; Gouda, M. Characterization and corrosion behavior of vanadium-based conversion coating on AZ31 magnesium alloy. *Mater. Today Proc.* **2022**, *62*, 611–614. <https://doi.org/10.1016/j.matpr.2022.03.618>.
31. Hafeez, M.; Farooq, A.; Zang, A.; Saleem, A.; Deen, K. Phosphate chemical conversion coatings for magnesium alloys: A review. *J. Coat. Technol. Res.* **2020**, *17*, 827–849. <https://doi.org/10.1007/s11998-020-00335-2>.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.