

Article

Effects of Solvothermal Temperature and Time on Microstructure and Corrosion Resistance of ZIF-8-Modified Micro-Arc Oxidation Coating on 6063 Aluminum Alloy

Haowu Li, Rongjun Yang, Weilin Chen, Weizhou Li *  and Deli Shen *

Fujian Provincial Key Laboratory of Functional Materials and Applications, Xiamen Key Laboratory for Powder Metallurgy Technology and Advanced Materials, School of Materials Science and Engineering, Xiamen University of Technology, Xiamen 361024, China; lihaowu_edu2022@163.com (H.L.); 2322161052@stu.xmut.edu.cn (R.Y.); 2422161008@stu.xmut.edu.cn (W.C.)

* Correspondence: wzli@xmut.edu.cn (W.L.); henryshen@126.com (D.S.); Tel.: +86-19859192880 (W.L.); +86-15659791163 (D.S.)

Abstract

ZIF-8-modified micro-arc oxidation (MAO) coatings have attracted considerable attention for improving the corrosion resistance of aluminum alloys, owing to their combined barrier and chemical protection effects. In this work, ZIF-8/MAO composite coatings were fabricated via in situ solvothermal growth, and the effects of solvothermal temperature and time on coating evolution and corrosion performance were systematically investigated. The coatings were characterized by field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FT-IR). The results show that increasing the solvothermal temperature promotes ZIF-8 formation, which may be related to enhanced coordination reactions and particle growth. Prolonging the solvothermal time induces a transition from ZnO-dominated coatings at 8 h to ZIF-8-dominated structures at 16–24 h, whereas unconverted ZnO is still detected after prolonged growth. The in situ-grown ZIF-8 particles cover the MAO surface and contribute to the sealing of surface micropores and cracks, forming a more compact composite barrier structure. The reduced coating performance at 220 °C or after 32 h may be associated with excessive particle refinement, local structural imperfections, or reduced coating integrity under prolonged or high-temperature solvothermal conditions. Electrochemical impedance spectroscopy (EIS) results reveal that the composite coating exhibits a charge transfer resistance more than one order of magnitude higher than that of the bare MAO coating, indicating significantly enhanced barrier protection. These findings demonstrate that in situ-grown ZIF-8 is an effective strategy for improving the corrosion resistance of MAO coatings on aluminum alloys.



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1. Introduction

Micro-arc oxidation (MAO) is a well-established and highly efficient surface modification technique, which has been extensively employed for valve metals (e.g., Al, Mg, Ti, Zr, and Nb), as well as their corresponding alloys and composites, to realize remarkable improvement in their surface properties [1–3]. However, a critical limitation of MAO coatings arises from their inherent porosity and microcracks. These structural defects originate

from the intricate physicochemical processes inherent in the MAO procedure, including dielectric breakdown during electrical discharge, the evolution of gaseous byproducts, and the rapid solidification of in situ-generated molten oxide phases [4]. Consequently, these structural imperfections act as preferential channels for the penetration and diffusion of corrosive media, thereby considerably impairing the long-term corrosion protection performance of coated metallic components.

To mitigate this critical limitation, sealing the porous MAO layer is regarded as a promising strategy. In this context, zeolitic imidazolate frameworks (ZIFs) emerge as an attractive candidate, owing to their outstanding properties, including a high specific surface area, tunable porosity, and exceptional chemical/thermal stability [5,6]. Structurally, ZIF-8 is composed of Zn^{2+} ions coordinated with 2-methylimidazole linkers [7,8]. Compared with most other metal–organic frameworks (MOFs), ZIF-8 exhibits distinct advantages, such as simpler and more flexible synthesis protocols. This unique combination of properties has spurred extensive research on ZIF-8-based materials in various forms (such as powders, colloids, thin films, and membranes) for a wide range of applications [9], among which corrosion protection has emerged as a novel focus. For instance, Chen et al. [10] fabricated a D-cys/Ag@ZIF-8 (DAZ-8) coating via an immersion method, which significantly inhibited corrosion on carbon steel. Moreover, alternative fabrication strategies have been explored, including secondary growth methods involving seeding followed by solvothermal synthesis [11], and microwave-assisted techniques for seed layer formation and growth [12,13].

Other strategies, like homologous metal induction (e.g., converting pre-deposited ZnO to ZIF-8 via vapor-phase reaction [14]), rely on sustained ion release from the substrate. Notably, it is worth noting that the in situ growth method has demonstrated considerable potential for constructing ZIF-based composite coatings on MAO-treated surfaces. Jin et al. [15] successfully fabricated LDH/ZIF-8 hybrid films on an MAO-coated magnesium alloy, wherein Zn^{2+} ions derived from the solvothermally synthesized LDH layer acted as nucleation sites for ZIF-8 crystallization. This ZIF-8 layer effectively sealed intergranular defects in the LDH, significantly enhancing barrier properties and reducing corrosion current density by several orders of magnitude. Similarly, Jiang et al. [16] developed in situ ZIF composite coatings on MAO-treated Mg alloy, which exhibited excellent hydrophobicity, self-cleaning performance, and significantly enhanced corrosion resistance. This improvement can be attributed to the coating's structural integrity, strong interfacial adhesion, and efficient defect-sealing capability inherent to the in situ nucleation-growth mechanism [15,17].

Despite these notable advancements, current research on ZIF-8/MAO composite coatings has predominantly centered on Mg alloy substrates. It should be noted that there is little research concerning the application and corrosion protection properties of such in situ-grown composite coatings on aluminum alloys, especially the widely utilized 6063 alloy [18]. Furthermore, while the inherent micropores of the MAO layer pose a challenge for corrosion resistance, they also offer a unique advantage: they can serve as mechanical interlocking sites, potentially enhancing the adhesion between a subsequently grown functional layer (like ZIF-8) and the substrate [17,19].

In this work, ZIF-8 coatings were fabricated on MAO-treated 6063 aluminum alloy substrates via an in situ growth method. Although extensive research has been conducted on MAO-based composite coatings and MOF modification strategies, the interfacial evolution behavior and structure–property relationship of in situ-grown ZIF-8 on MAO layers remain insufficiently understood, particularly with respect to their influence on corrosion protection performance. To address this research gap, this study systematically investigates the morphological evolution and structural characteristics of ZIF-8/MAO composite coat-

ings under different solvothermal conditions. The novelty of this work lies in revealing the phase transformation behavior and defect-sealing mechanism of ZIF-8 grown in situ on the surface of MAO coatings, and in correlating these structural features with the enhanced corrosion resistance of these coatings.

2. Materials and Methods

The 6063 Al alloy with dimensions of 20 mm × 15 mm × 3 mm, provided by China Aluminum Materials Application Research Institute Co., Ltd., Beijing, China, was utilized as the substrate, and its chemical composition is presented in Table 1. The samples were ground with SiC abrasive papers from (180–800 grit, Hengyu, Jinhua, China), rinsed in deionized water, anhydrous ethanol, and acetone step by step, and then dried at room temperature. Deionized water was prepared using a deionized water maker supplied by Shanghai Liding Water Treatment Equipment Co., Ltd. (Shanghai, China). Analytical-grade absolute ethanol and acetone were purchased from Xilong Scientific Co., Ltd. (Shantou, China). Then, the MAO process was performed using the YS9000D-60020 dual-pulse micro-arc oxidation equipment (Shanghai Yisheng, Shanghai, China). The samples were immersed in a silicate electrolyte prepared with reagents (10 g/L Na₂SiO₃, 2 g/L KOH, and 2 g/L NaOH) from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), all of analytical grade. The 6063 Al alloy samples were coated under the constant current mode (8 A/dm²) for 25 min with a frequency of 200 Hz and a duty ratio of 10%. After the MAO coating preparation, the samples were washed with deionized water to remove the residual electrolyte on the surface and then dried for future use.

Table 1. Chemical composition of 6063 aluminum alloy (wt.%).

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
0.2–0.6	≤0.35	≤0.1	≤0.1	0.45–0.9	≤0.1	≤0.1	≤0.1	balance

A precursor solution was prepared by dissolving 0.59 g of Zn(NO₃)₂·6H₂O, 0.135 g of HCOONa, and 0.245 g of 2-methylimidazole in 30 mL of methanol under stirring. The cleaned MAO-treated 6063 Al alloy substrate was then immersed in the solution and transferred to a Teflon-lined autoclave. Analytical-grade Zn(NO₃)₂·6H₂O was supplied by Sinopharm Chemical Reagent Co., Ltd. HCOONa, methanol and 2-methylimidazole were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). The stainless steel autoclave (Model LC-KH-100) with PTFE liner was obtained from Shanghai Lichen Instrument Technology Co., Ltd. (Shanghai, China). To investigate the effects of solvothermal conditions, samples were prepared at 100–220 °C for 24 h and labeled MZ100, MZ140, MZ180, and MZ220, respectively. Additional samples were prepared at 180 °C for 8–32 h and labeled MZ8h, MZ16h, MZ24h, and MZ32h, respectively. After reaction, all samples were rinsed with methanol and dried at ambient temperature for characterization. The sample labels and experimental conditions are listed in Table 2.

Table 2. Sample codes and corresponding solvothermal treatment conditions.

Sample Code	Solvothermal Temperature (°C)	Solvothermal Time (h)	Description
MAO	/	/	Bare MAO coating without ZIF-8 modification
MZ100	100	24	ZIF-8/MAO coating prepared at 100 °C for 24 h

Table 2. Cont.

Sample Code	Solvothermal Temperature (°C)	Solvothermal Time (h)	Description
MZ140	140	24	ZIF-8/MAO coating prepared at 140 °C for 24 h
MZ180/MZ24h	180	24	ZIF-8/MAO coating prepared at 180 °C for 24 h
MZ220	220	24	ZIF-8/MAO coating prepared at 220 °C for 24 h
MZ8h	180	8	ZIF-8/MAO coating prepared at 180 °C for 8 h
MZ16h	180	16	ZIF-8/MAO coating prepared at 180 °C for 16 h
MZ32h	180	32	ZIF-8/MAO coating prepared at 180 °C for 32 h

A ZIF-8-modified micro-arc oxidation (MAO) coating was fabricated on the substrate. The surface and cross-sectional morphology of the coatings were examined using a Sigma 500 scanning electron microscope (SEM, Zeiss, Oberkochen, Germany). Chemical composition analysis was performed via an energy-dispersive spectrometer (EDS) attached to the SEM. Phase composition was analyzed by X-ray diffraction (XRD) using a SmartLab 3 KW diffractometer (XRD, Rigaku Corporation, Akishima, Japan) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 100 mA. The scan range was $2\theta = 10^\circ$ to 85° with a step size of 0.02° and a scan speed of $4^\circ/\text{min}$. The molecular structure and chemical bonding of the coating were characterized by Fourier-transform infrared spectroscopy (FT-IR) using a BRUKER ALPHA spectrometer (Bruker Optics, Ettlingen, Germany). Samples for FT-IR were prepared using the KBr pellet method with spectral grade KBr, and spectra were acquired over a wavenumber range of 400 to 2000 cm^{-1} with 64 scans. Data processing was conducted using the OMNIC software suite (Version 8.2, Thermo Fisher Scientific, Waltham, MA, USA). Corrosion resistance of the samples was assessed using an electrochemical workstation to test the potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). The PDP test was conducted with a scan rate of 2 mV/s . The corrosion potential (E_{corr} (V)) and the corrosion current density (I_{corr} ($\text{A}\cdot\text{cm}^{-2}$)) were obtained by Tafel extrapolation in the strongly polarized region. Combined with the Stern–Geary equation, the corrosion rate CR ($\text{mm}\cdot\text{y}^{-1}$) can be calculated as follows:

$$CR = \frac{MI_{\text{corr}}}{n\rho F} \quad (1)$$

where M is the molar mass of the metal (g/mol), n is the valence of the metal ion, ρ is the density of the metal (g/cm^3), and F is the Faraday constant ($96,485 \text{ C/mol}$).

EIS measurements were conducted in 3.5 wt% NaCl solution using the coated sample as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum plate as the counter electrode. The scanning frequency was in the range of 10^5 – 10^{-2} Hz , and the sinusoidal perturbation was 10 mV . The obtained EIS data were fitted and analyzed by Zview software (Version 3.5d, Scribner Associates Inc., Southern Pines, NC, USA). The area of the sample for testing was 1 cm^2 .

3. Results

3.1. Solvothermal Temperature

3.1.1. Morphology

The surface morphologies of the pristine MAO coating and ZIF-8 coatings prepared at different temperatures are presented in Figure 1. Systematic SEM characterization at four synthesis temperatures (100, 140, 180, and 220 °C) reveals the critical role of temperature in governing crystal growth. As shown in Figure 1a, the unmodified MAO coating exhibits prominent volcano-like structures with numerous micropores and microcracks, which are typical characteristics of MAO coatings. At relatively low temperatures (100 and 140 °C), fine particles with sizes of 1–2 µm aggregate into irregular clusters, showing high-surface roughness and poorly defined boundaries (Figure 1b,c). These morphological characteristics are consistent with the crystal growth behavior of ZnO [18–20], indicating that zinc ions primarily undergo hydrolysis to form ZnO nuclei instead of coordinating with ligands to construct a metal–organic framework (MOF) in this temperature range. A distinct morphological transition is observed at 180 °C (Figure 1d). It is shown that particle size increases remarkably to 2–4 µm, forming well-defined hexahedral crystals with smooth surfaces. This distinctive tetrahedral morphology indicates the onset of ZIF-8 crystallization, which is driven by the enhanced coordination between Zn²⁺ ions and 2-methylimidazole ligands [21–23]. Notably, the morphological transition observed in Figure 1 demonstrates the essential role of temperature in promoting the critical phase transformation from ZnO to ZIF-8 on the MAO coating's surface. This transformation confirms that an elevated temperature overcomes the activation energy barrier and accelerates the nucleation of ZIF-8, thereby driving the process toward successful ZIF-8 formation, which is highly likely to result in a continuous ZIF-8 film [13,24–26].

EDS distribution maps of MAO/ZIF-8 coatings fabricated at various reaction temperatures are presented in Figure 2, and the corresponding elemental compositions are summarized in Table 3. The MAO substrate mainly contains Al (39.3 wt.%) and O (60.7 wt.%), which is consistent with an alumina-based ceramic layer. For MZ100 and MZ140, high Zn contents of 73.8–75.6 wt.% and O contents of 18.4–19.7 wt.% are observed, while only small amounts of C and N are detected, indicating the predominant presence of ZnO at lower temperatures. In contrast, MZ180 shows a marked compositional transition, with a sharp decrease in Zn content to 10.3 wt.% and substantial increases in C and N contents to 50.5 wt.% and 19.6 wt.%, respectively. This change is attributed to the transformation from ZnO-rich products to ZIF-8-rich structures, as supported by the increased C and N signals, which are consistent with the formation of the 2-methylimidazole-based ZIF-8 framework [27]. For MZ220, the Zn content increases to 39.8 wt.%, while the C and N contents decrease to 32.0 wt.% and 13.5 wt.%, respectively, with a detectable oxygen signal of 14.7 wt.%. These compositional features suggest that the coating formed at 220 °C still contains oxygen-bearing species, which may be associated with incompletely converted ZnO precursors, exposed MAO oxide regions, or surface oxygen-containing species. Overall, the SEM observations and EDS results indicate that increasing the synthesis temperature promotes the formation of ZIF-8-containing coatings, although an excessively high temperature may alter the elemental composition and coating structure.

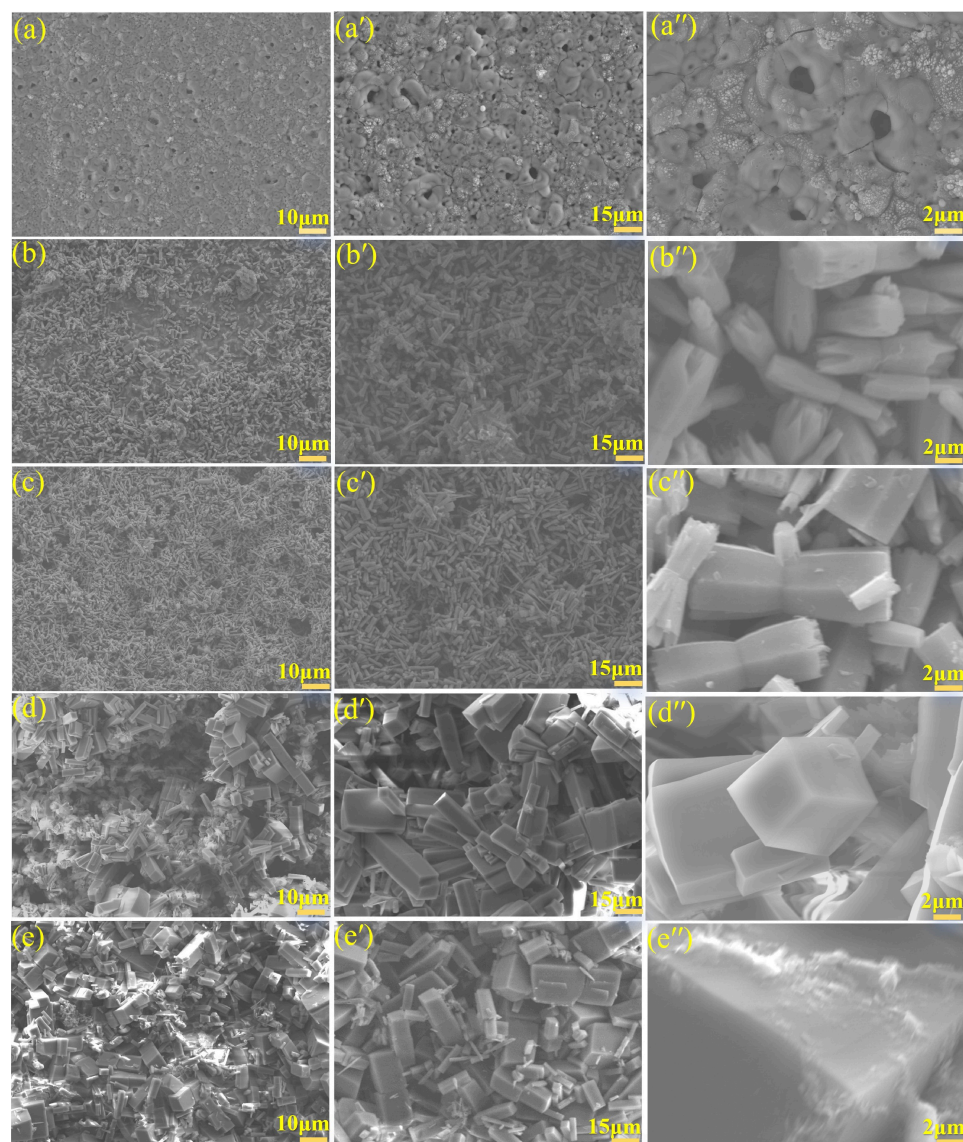


Figure 1. Surface morphology of blank and temperature-dependent ZIF-8 coatings: (a,a',a'') MAO, (b,b',b'') MZ100, (c,c',c'') MZ140, (d,d',d'') MZ180, and (e,e',e'') MZ220.

Table 3. EDS elemental compositions obtained from the selected area-scan regions marked in Figure 1b'–e'.

Sample	Elemental Content (wt.%)				
	Al	O	Zn	C	N
MAO	39.3	60.7	/	/	/
MZ100	/	19.7	73.8	5.3	1.2
MZ140	/	18.4	75.6	4.5	1.4
MZ180	/	19.6	10.3	50.5	19.6
MZ220	/	14.7	39.8	32.0	13.5

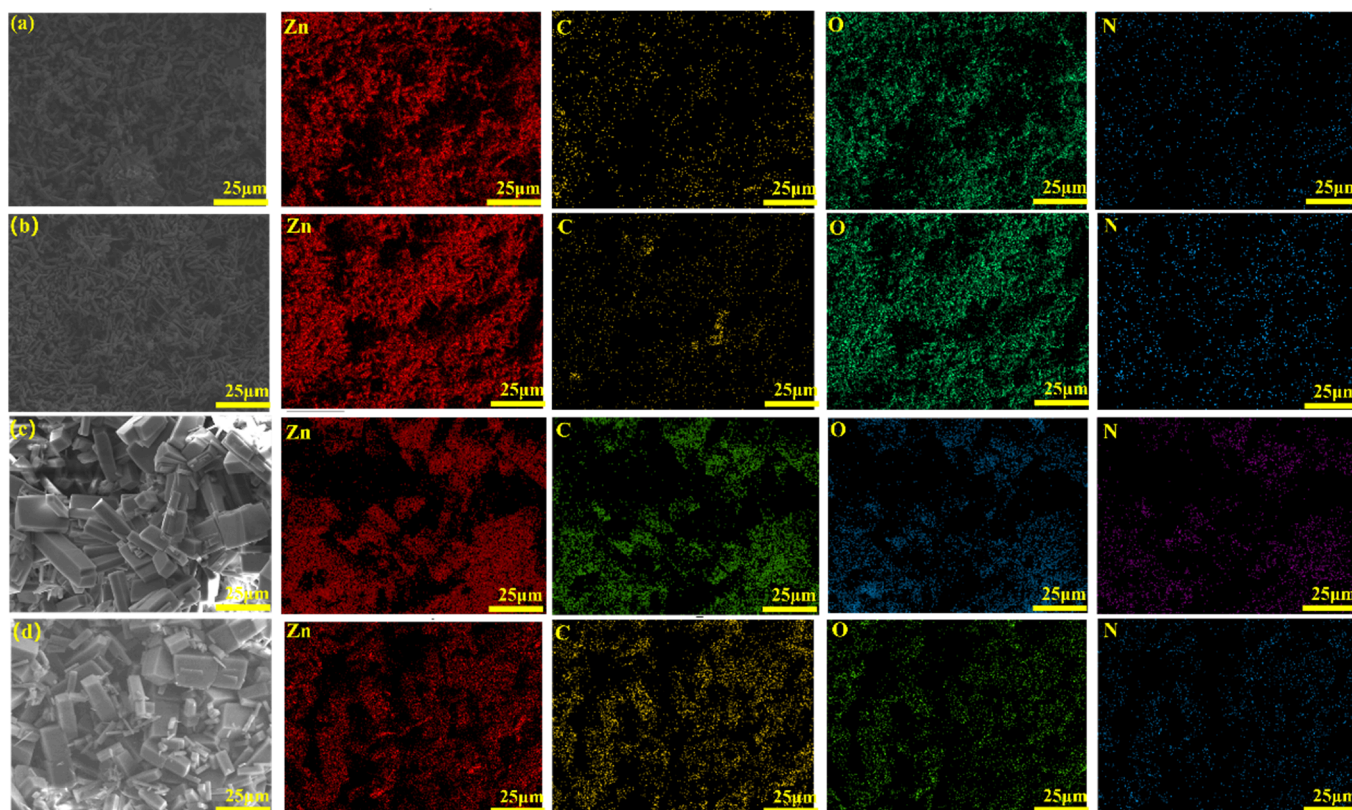


Figure 2. EDS distribution maps of MAO/ZIF-8 coatings prepared at different reaction temperatures: (a) MZ100, (b) MZ140, (c) MZ180, and (d) MZ220.

3.1.2. Phase Compositions

Figure 3 presents the XRD patterns of the pristine MAO coating and MAO/ZIF-8 composite coatings. As can be observed in the XRD patterns, the composite coatings synthesized at solvothermal temperatures of 100 °C and 140 °C are predominantly composed of γ - Al_2O_3 and ZnO phases. The diffraction peaks corresponding to metallic aluminum originate from the permeable microporous structure of the MAO coating, which allows X-rays to penetrate into the underlying substrate [1,28]. Within the 2θ range of 30–36°, distinct ZnO diffraction peaks at 31.7° and 34.4° exhibit a gradual increase in intensity by the MZ100 to MZ140 samples. This intensity increase reflects temperature-dependent nucleation and crystal growth mechanisms. Notably, the ZnO diffraction peaks are significantly intensified for the MZ140 sample, indicating thermally activated oxidation of zinc precursors. Characteristic ZIF-8 diffraction peaks emerge at temperatures above 100 °C, with the most prominent peak located at $2\theta = 10.3^\circ$. The resolution of these ZIF-8 characteristic peaks is significantly enhanced at 180 °C, confirming the improved crystallinity of ZIF-8 with increasing synthesis temperature. Specifically, the predominant peak at 10.3° corresponds to the (002) crystal plane of ZIF-8, suggesting substrate-induced preferential growth along the [002] crystallographic orientation. Such orientation-selective growth is facilitated by elevated temperatures and extended reaction durations. This underscores an advantage of solvothermal synthesis over solvothermal methods: the constrained nucleation kinetics and milder reaction environment promote the formation of dense, ordered ZIF-8 architectures with defined crystallographic orientations.

As shown in Figure 4, the Fourier-transform infrared spectra of the pristine MAO coating and MAO/ZIF-8 composite coatings track the evolution of vibrational modes associated with imidazole coordination. At 100 °C for the MZ100 sample, no characteristic vibrational bands related to imidazole ligands are detected, which is consistent with that

of the unmodified MAO layer, confirming the absence of ZIF-8 formation. This result aligns with the EDS (Table 3) and XRD (Figure 3) analyses, which collectively verify a ZnO-dominated surface for the MZ100 sample. Elevating the solvothermal temperature to 140 °C (MZ140) leads to the emergence of characteristic vibrational peaks of imidazole ligands: 1560 cm^{-1} (symmetric stretching vibration of C=N bonds), 1370 cm^{-1} (coupled antisymmetric stretching vibration of C-N bonds and imidazole ring bending), 1140 cm^{-1} (in-plane breathing vibration of imidazole rings), 1000 cm^{-1} (out-of-plane breathing vibration of imidazole rings), and 700 cm^{-1} (wagging vibration of C-H bonds). Notably, the diagnostic absorption band of the Zn-N coordination bond at 420 cm^{-1} remains undetected, indicating incomplete formation of ZIF-8 at this temperature. However, a further increase in solvothermal temperature to 180 °C (MZ180) and 220 °C (MZ220) induces the distinct appearance of the 420 cm^{-1} absorption band, confirming the formation of the Zn-N coordination bond and successful coordination between Zn^{2+} ions and imidazole nitrogen atoms [21,29–32]. Importantly, the intensity of all imidazole-related vibrational bands gradually enhances with increasing solvothermal temperature: the bands are undetectable in MZ100, resolved but lacking the Zn-N characteristic band in MZ140, and further intensified (including the 420 cm^{-1} Zn-N band) in MZ220 compared to MZ180. This systematic intensity variation collectively highlights the critical regulatory role of solvothermal temperature in modulating the growth kinetics and crystallinity of ZIF-8.

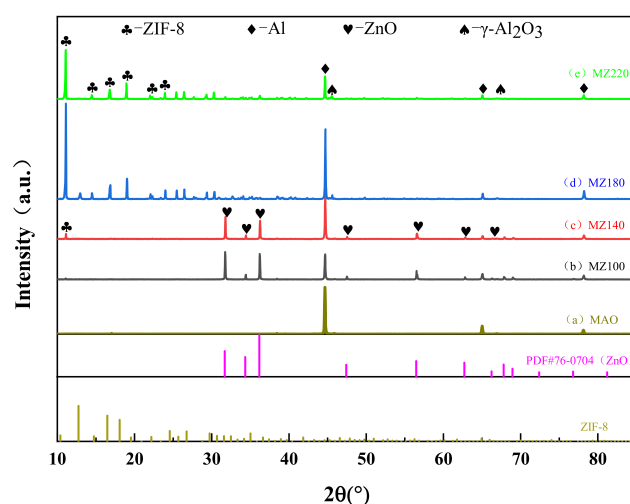


Figure 3. XRD patterns of MAO coating and MAO/ZIF-8 composite coating.

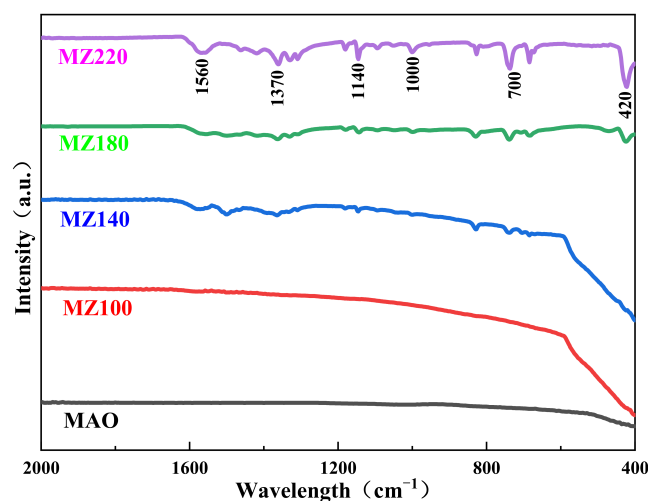


Figure 4. FT-IR spectra of MAO coating and MAO/ZIF-8 coatings.

3.1.3. Corrosion Resistance

Since the protective performance of coatings is directly governed by their microstructural features, electrochemical measurements were conducted to quantitatively evaluate their corrosion behavior. It should be noted that, due to the passive/coating layer on the aluminum alloy surface, the corrosion current density and corrosion rate obtained from polarization fitting may contain certain uncertainties. Therefore, these parameters are mainly used for comparative evaluation under identical testing conditions, and the corrosion protection performance is further supported by the EIS results. The EIS test results of MAO/ZIF-8 coatings prepared at different solvothermal temperatures are displayed in Figure 5, and the corresponding equivalent circuit diagram is shown in Figure 6. Table 4 summarizes the electrochemical impedance spectroscopy fitting results obtained from Zview software, listing key parameters such as film resistance (R_m) and charge transfer resistance (R_{ct}). Although the absolute R_m values are much smaller than the corresponding R_{ct} values, they still exhibit a clear dependence on the solvothermal processing conditions. The R_m value increases from 183.7 Ω for the bare MAO coating to 185.0 Ω , 190.9 Ω , and 198.3 Ω for MZ100, MZ140, and MZ180, respectively, suggesting that the in situ growth of ZIF-8 gradually improves the compactness and barrier properties of the coating film. This trend is consistent with the SEM observations and electrochemical results, indicating that appropriate ZIF-8 growth contributes to the coverage of surface defects in the MAO coating. However, when the solvothermal temperature is further increased to 220 $^{\circ}\text{C}$, the R_m value decreases, implying that an excessive growth temperature may weaken the coating integrity or introduce local structural imperfections. Compared with the moderate variation in R_m , the much larger increase in R_{ct} indicates that the enhanced corrosion resistance mainly originates from the improved resistance to interfacial charge transfer and electrolyte penetration. Compared to the bare MAO sample ($R_{ct} = 1.69 \times 10^5 \Omega \cdot \text{cm}^2$), the MZ100 coating ($R_{ct} = 1.76 \times 10^5 \Omega \cdot \text{cm}^2$) exhibited a negligible improvement in corrosion resistance. This modest enhancement can be directly attributed to its microstructure characteristics: at 100 $^{\circ}\text{C}$, merely a superficial layer of densely aggregated ZnO nanoparticles with high-surface roughness and poorly defined boundaries was formed (Figure 1b,c). Such a porous and discontinuous surface morphology, combined with the concurrent dissolution of the underlying MAO layer under the alkaline solvothermal environment, failed to establish an effective barrier. A significant enhancement in corrosion resistance was achieved at 140 $^{\circ}\text{C}$ (MZ140, $R_{ct} = 8.24 \times 10^5 \Omega \cdot \text{cm}^2$). The elevated R_{ct} value is consistent with the more uniform and extensive ZnO coverage observed via SEM (Figure 1c) and the enhanced ZnO diffraction intensity in the XRD pattern (Figure 3), which collectively contribute to a denser physical barrier compared to the sample prepared at 100 $^{\circ}\text{C}$. Notably, the charge transfer resistance reached its maximum at 180 $^{\circ}\text{C}$ (MZ180, $R_{ct} = 2.21 \times 10^6 \Omega \cdot \text{cm}^2$), representing an order-of-magnitude increase relative to the bare MAO coating. This optimum corrosion performance correlates with a distinct microstructural transition: SEM imaging reveals the formation of well-faceted, smooth-surfaced hexahedral crystals, indicative of the onset of ZIF-8 crystallization (Figure 1d). This conclusion is further confirmed by a sharp increase in carbon and nitrogen contents (C/N) in the EDS analysis (Table 3), the XRD test results in Figure 3, and the detection of C-N and Zn-N bonds via FT-IR in Figure 4. The resulting continuous and compact ZIF-8 layer acts as a highly effective barrier against electrolyte penetration. By contrast, further elevating the solvothermal temperature to 220 $^{\circ}\text{C}$ (MZ220) resulted in reduced R_m and R_{ct} values, indicating a deterioration in barrier properties. Although the SEM images show a fully covered surface composed of uniform and highly crystalline prismatic ZIF-8 crystals (Figures 1e and 3), EDS analysis reveals a relatively high Zn content (39.8 wt.%) and a detectable oxygen signal (14.7 wt.%). Since oxygen is not a constituent element of the ZIF-8 framework, this oxygen signal may originate from

incompletely converted ZnO precursors, exposed MAO oxide regions, or surface-adsorbed oxygen-containing species. Collectively, the EIS results, combined with the systematic microstructural and compositional characterizations (SEM, EDS, XRD, and FT-IR), demonstrate the following: (1) solvothermal synthesis effectively improves the corrosion resistance of MAO coatings through the in situ integration of ZIF-8; (2) solvothermal temperature serves as the critical parameter governing coating performance, primarily by regulating the crystallization behavior, phase composition, and morphological integrity of the ZIF-8 layer. Optimal protective performance is attained at 180 °C, where a favorable balance among morphological continuity, crystalline perfection, and chemical stability is achieved.

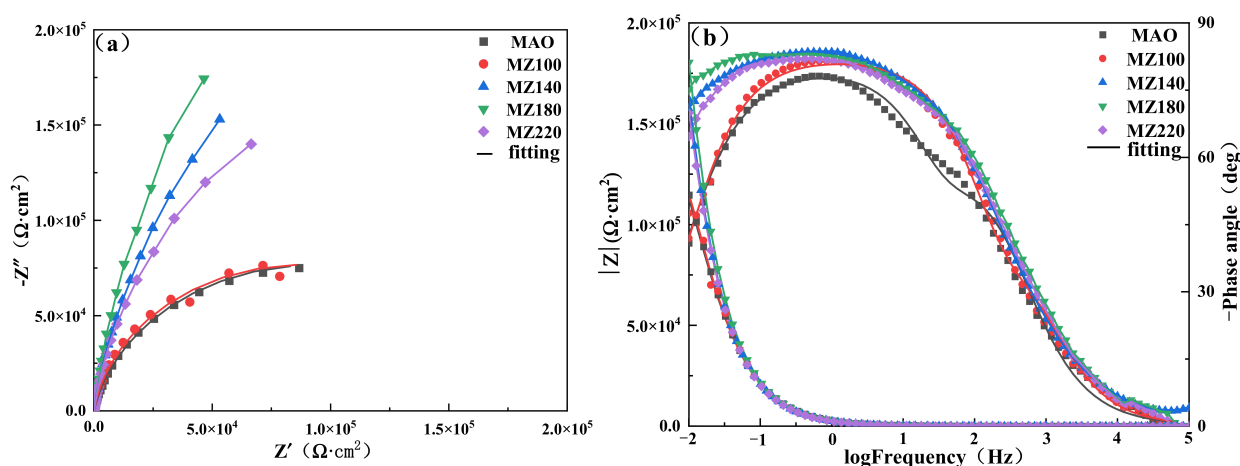


Figure 5. EIS test results of MAO/ZIF-8 coating prepared at different solvothermal temperatures: (a) Nyquist diagram; (b) Bode diagram.

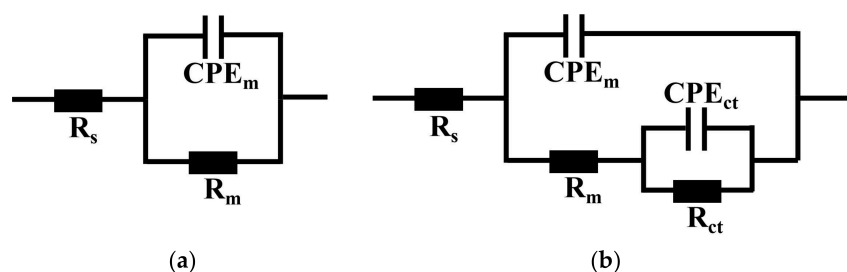


Figure 6. The equivalent circuit diagrams of different samples: (a) blank MAO, (b) ZIF-8 modified MAO coating.

Table 4. EIS fitting data of MAO coating and MAO/ZIF-8 coatings.

Sample	MAO	MZ100	MZ140	MZ180	MZ220
R_s	11.8	11.0	12.5	11.8	12.6
R_m	183.7	185.0	190.9	198.3	190.7
R_{ct}	1.69×10^5	1.76×10^5	8.24×10^5	2.21×10^6	6.09×10^5

Figure 7 depicts the potentiodynamic polarization curves of the composite coatings, and Table 5 shows the corrosion potential and corrosion current density of various coatings. The polarization curves were recorded without explicit IR compensation; therefore, the obtained electrochemical parameters were mainly used for comparative evaluation under identical testing conditions. I_{corr} measurements are generally carried out to evaluate the corrosion rate of a coating. The lower the I_{corr} , the better the corrosion resistance; in contrast, E_{corr} reflects the corrosion thermodynamic tendency of a coating and is not used for anti-corrosion performance evaluation [33]. The bare MAO coating exhibits a corrosion

potential of -0.004 V, a corrosion current density of $1.60 \times 10^{-7} \text{ A}\cdot\text{cm}^{-2}$, and a calculated corrosion rate (CR) of $1.74 \times 10^{-3} \text{ mm}\cdot\text{y}^{-1}$. At lower solvothermal temperatures, the corrosion protection performance improved marginally. The MZ100 coating showed a slight positive shift in E_{corr} to -0.002 V and a reduction in I_{corr} of $1.42 \times 10^{-7} \text{ A}\cdot\text{cm}^{-2}$ ($\text{CR} = 1.55 \times 10^{-3} \text{ mm}\cdot\text{y}^{-1}$), which is consistent with the formation of a superficial, porous ZnO layer observed via SEM. A more significant enhancement in corrosion resistance was achieved at 140°C , where E_{corr} shifted positively to 0.008 V and I_{corr} decreased to $6.43 \times 10^{-8} \text{ A}\cdot\text{cm}^{-2}$ ($\text{CR} = 7.00 \times 10^{-4} \text{ mm}\cdot\text{y}^{-1}$). This improvement is attributable to the growth of a denser, yet still ZnO-dominated particulate layer on the MAO surface. The optimal corrosion resistance was attained at 180°C , which exhibited the most noble E_{corr} of 0.021 V, the lowest I_{corr} of $1.86 \times 10^{-8} \text{ A}\cdot\text{cm}^{-2}$, and a minimal CR of $2.03 \times 10^{-4} \text{ mm}\cdot\text{y}^{-1}$. This superior performance is directly correlated with the complete microstructural transition to a continuous and well-crystallized ZIF-8 layer, as confirmed by SEM, EDS, XRD, and FT-IR, which acts as an effective diffusion barrier against corrosive electrolytes. However, further increasing the solvothermal temperature to 220°C led to a noticeable decline in corrosion protection performance ($E_{\text{corr}} = 0.007$ V, $I_{\text{corr}} = 6.81 \times 10^{-8} \text{ A}\cdot\text{cm}^{-2}$, $\text{CR} = 7.42 \times 10^{-4} \text{ mm}\cdot\text{y}^{-1}$). Despite the highly crystalline and fully covered ZIF-8 surface observed by SEM, the relatively high Zn content and detectable oxygen signal revealed by EDS may indicate incomplete conversion of the ZnO precursor or the presence of oxygen-containing species. These compositional features may affect the long-term barrier performance of the composite coating under high-temperature solvothermal conditions.

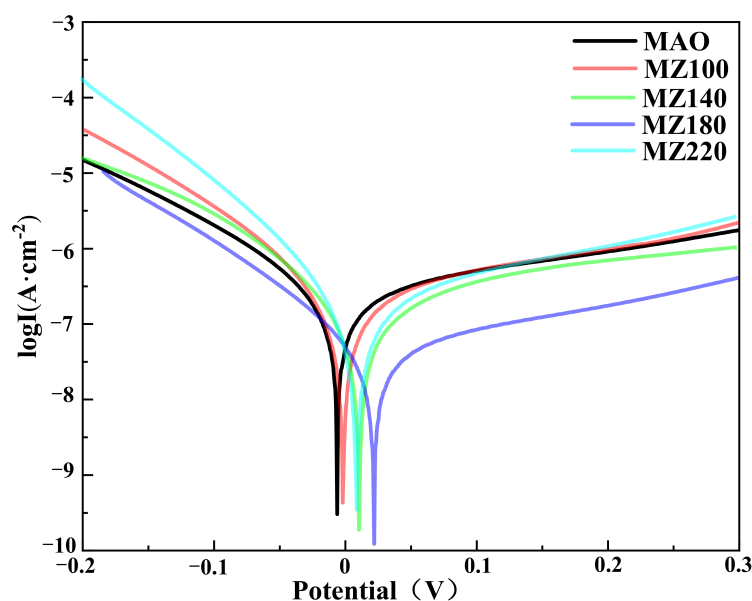


Figure 7. Polarization curves of of MAO coatings and MAO/ZIF-8 coatings prepared at different solvothermal temperatures.

Table 5. Polarization curve-fitting data of MAO coating and MAO/ZIF-8 composite coatings.

Sample	E_{corr} (V)	I_{corr} (A/cm^2)	CR (mm/y)
MAO	-0.004	1.60×10^{-7}	1.74×10^{-3}
MZ100	-0.002	1.42×10^{-7}	1.55×10^{-3}
MZ140	0.008	6.43×10^{-8}	7.00×10^{-4}
MZ180	0.021	1.86×10^{-8}	2.03×10^{-4}
MZ220	0.007	6.81×10^{-8}	7.42×10^{-4}

3.2. Solvothermal Duration

3.2.1. Morphology

In addition to temperature, solvothermal duration constitutes another pivotal parameter governing the growth of ZIF-8. This section systematically investigates the temporal evolution of the MAO/ZIF-8 composite coating and the effect of reaction duration on its structure and morphology. As depicted in Figure 8a,a', the surface of the MZ8h coating is predominantly covered with small, irregular ZnO nanoparticles, which are dispersedly distributed without forming well-defined columnar crystalline structures. Figure 8b,b' illustrates the surface morphology of the MZ16h coating, in which incipient columnar/rod-like ZnO structures emerge, and hexahedral crystalline particles of approximately 1–4 μm in size present more regular geometric shapes with smooth surfaces. At the duration of 24 h (MZ24h, Figure 8c), the ZnO crystals further enlarge to 2–6 μm while retaining well-defined hexahedral geometry. When the solvothermal duration is extended from 24 to 32 h, a pronounced morphological change in ZIF-8 is observed. The 24 h sample exhibits relatively large, highly crystalline, and well-defined columnar or hexagonal block-like crystals, suggesting sufficient crystal growth under this condition. In contrast, the 32 h sample shows refined and dispersed submicrometer rod-like or flower-like aggregates, accompanied by an obvious reduction in crystal size. This morphological change may be associated with excessive solvothermal growth, which could affect the structural compactness and protective performance of the coating. This morphological transition is attributed to the dissolution–recrystallization process of ZIF-8: under prolonged solvothermal conditions, the large columnar crystals undergo dissolution due to partial framework collapse and ligand detachment, and the released Zn^{2+} ions and ligands reach supersaturation in the solution, thereby triggering secondary nucleation and generating a large number of fine nanocrystals. Simultaneously, environmental changes such as a decrease in solution pH and an imbalance in ligand concentration inhibit further growth of the small crystallites, ultimately resulting in the formation of fragmented flocculent structures. This process is essentially a kinetically dominated inverse Ostwald ripening, suggesting that the solvothermal stability of ZIF-8 exhibits a temporal threshold, with 24 h being identified as the optimal growth duration, beyond which structural degradation and morphological deterioration occur.

Surface morphology and EDS elemental distribution maps of ZIF-8/MAO composite coatings fabricated at different solvothermal reaction times are shown in Figure 9. As detailed in Table 6, EDS elemental analysis provides information on the compositional evolution of the MAO/ZIF-8 composite coatings at different solvothermal durations. The unmodified MAO coating mainly contains Al (39.3 wt.%) and O (60.7 wt.%), which is consistent with an alumina-based ceramic layer. For the MZ8h sample, relatively high O (43.0 wt.%) and Zn (18.8 wt.%) contents are observed, together with lower C (32.4 wt.%) and N (5.9 wt.%) contents. It should be noted that the stoichiometric Zn atomic ratio in ZnO is 1:1. Therefore, the detected O/Zn atomic ratio of approximately 2.3:1 should not be directly regarded as the stoichiometric ratio of ZnO. Instead, the relatively high O and Zn signals suggest the presence of ZnO-related species, while the excess oxygen may also originate from the underlying MAO oxide layer or oxygen-containing surface species. These results indicate that ZIF-8's formation is still limited at the early growth stage. When the reaction time is extended to 16 h, a significant compositional change is observed: the O content decreases sharply to 23.1 wt.%, accompanied by substantial increases in C and N contents to 49.1 wt.% and 23.1 wt.%, respectively. The increased C and N signals are consistent with the formation of the 2-methylimidazole-based ZIF-8 framework. Meanwhile, the Zn content decreases to 11.6 wt.%, suggesting the gradual transformation from ZnO-rich products to ZIF-8-rich structures. After 24 h of growth, the O content further decreases to 19.6 wt.%,

while the relatively high C and N contents indicate further development of the ZIF-8 phase and reduced contribution from ZnO-related species. However, in the MZ32h sample, the oxygen content increases to 23.5 wt.%, while the C and N contents slightly decrease to 48.6 wt.% and 16.5 wt.%, respectively. This compositional change may indicate the presence of oxygen-containing species or incompletely converted ZnO-related components within the predominantly ZIF-8-containing coating. Overall, prolonged solvothermal duration promotes a transition from ZnO-rich products to ZIF-8-rich structures. The 16–24 h period appears to be favorable for ZIF-8 growth, whereas further extension to 32 h may induce compositional changes and structural reorganization, which could affect the compactness and protective performance of the coating.

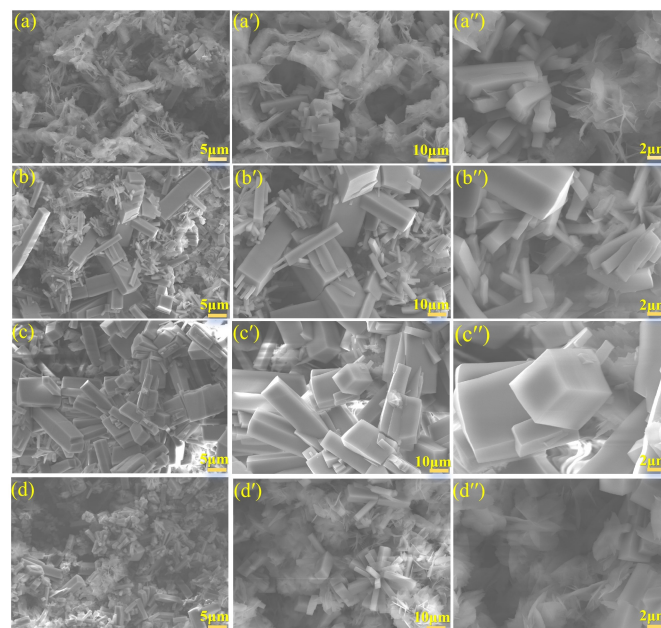


Figure 8. Surface morphology of MAO/ZIF-8 composite coatings prepared at different growth times: (a,a',a'') 8 h, (b,b',b'') 16 h, (c,c',c'') 24 h, and (d,d',d'') 32 h, respectively.

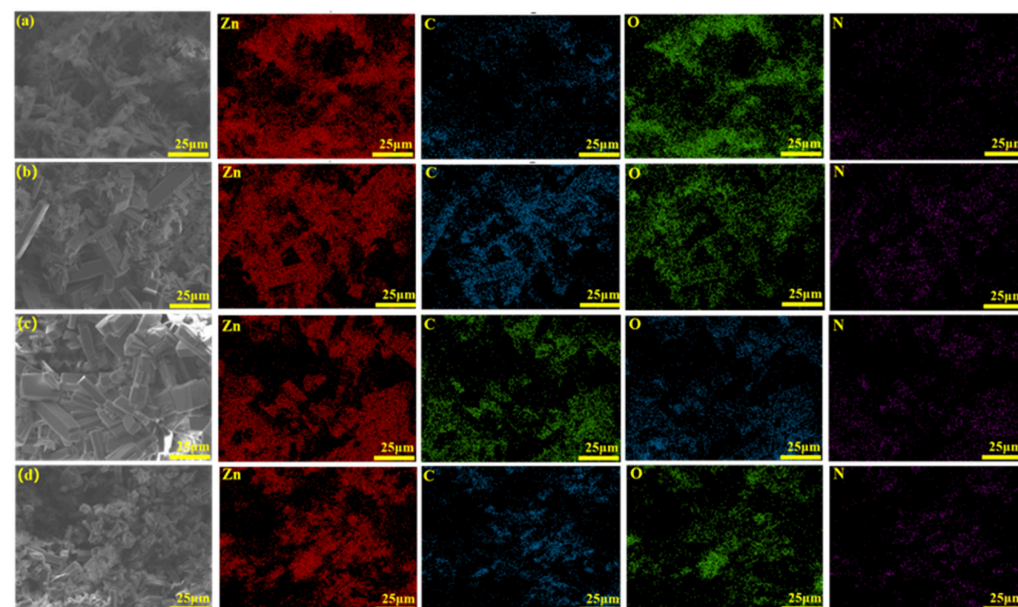


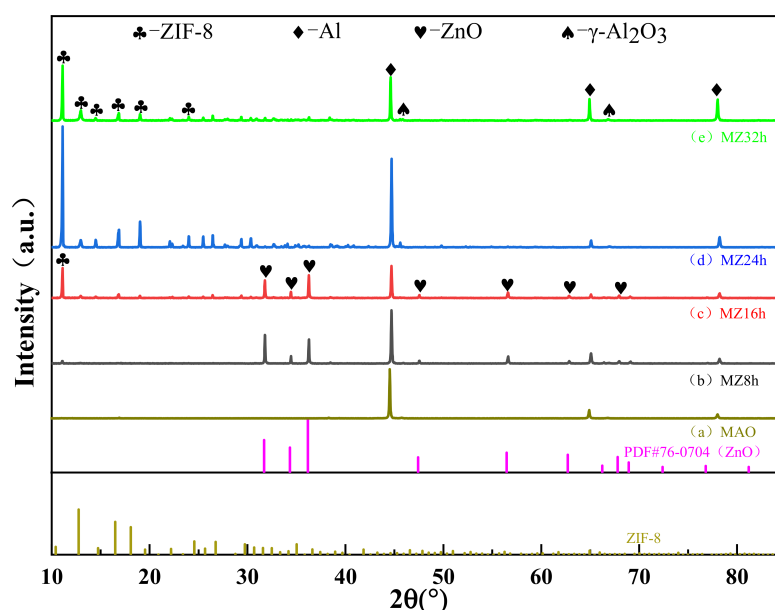
Figure 9. Surface morphology and EDS elemental distribution maps of ZIF-8/MAO composite coatings fabricated under different solvothermal reaction growth times: (a) 8 h, (b) 16 h, (c) 24 h, and (d) 32 h.

Table 6. EDS elemental compositions obtained from the selected area-scan regions marked in Figure 8a–d.

Sample	Elemental Content (wt.%)				
	Al	O	Zn	C	N
MAO	39.3	60.7	/	/	/
MZ8h	/	43.0	18.8	32.4	5.9
MZ16h	/	23.1	11.6	49.1	23.1
MZ24h	/	19.6	10.3	50.5	19.6
MZ32h	/	23.5	11.4	48.6	16.5

3.2.2. Phase Compositions

The morphological evolution described above implies the occurrence of a phase transformation process, which necessitates validation through XRD phase analysis. Figure 10 presents the XRD patterns of the MAO/ZIF-8 composite coatings prepared at different solvothermal durations. The intensity of the characteristic ZIF-8 diffraction peak located at $2\theta = 10.3^\circ$ exhibits an initial increase followed by a subsequent decrease with prolonged growth time. When the growth duration is shorter than 24 h, characteristic ZnO diffraction peaks at 31.7° (100) and 34.4° (002) are observed within the 2θ range of $30\text{--}36^\circ$, indicating the presence of unconverted ZnO in the coating at this stage. After 24 h of growth, the characteristic ZIF-8 peak at 10.3° reaches its maximum intensity, while the ZnO diffraction peaks are no longer detected. This variation indicates that under the 24 h solvothermal condition, amorphous phases and unreacted precursors are sufficiently consumed, and the ZIF-8 crystallites undergo continuous growth via the Ostwald ripening process, resulting in a more complete crystal structure and a significantly increased proportion of phase-pure ZIF-8. This result corroborates the conclusion established in the preceding section that a temperature of 180°C is favorable for ZIF-8 growth. However, when the growth duration is further extended to 32 h, the intensity of the characteristic peak at 10.3° decreases notably, which is consistent with the morphological deterioration observed in Figure 8d, suggesting that the excessive solvothermal duration triggers an inverse Ostwald ripening process, leading to structural degradation of the ZIF-8 framework.

**Figure 10.** XRD patterns of MAO/ZIF-8 composite coatings prepared at different growth times.

As illustrated in Figure 11, Fourier-transform infrared spectra were recorded for the pristine MAO coating and MAO/ZIF-8 composite coatings to identify the vibrational modes associated with imidazole coordination and to verify the successful formation of the ZIF-8 framework. The MAO coating exhibited no discernible absorption peaks within the 400–2000 cm^{-1} range, which is consistent with the chemical inertness of the inorganic alumina ceramic phase. In contrast, the MAO/ZIF-8 composite coating prepared at 180 °C displayed characteristic vibrational fingerprints attributable to ZIF-8: the absorption band at 1580 cm^{-1} was assigned to the asymmetric stretching vibration of C=N bonds; the band at 1370 cm^{-1} corresponded to the coupled symmetric stretching of C-N bonds and in-plane bending of the imidazole ring; the bands at 1140 cm^{-1} and 1000 cm^{-1} were attributed to the in-plane breathing vibration of the imidazole ring and the out-of-plane C-H twisting vibration, respectively; and the band at 700 cm^{-1} was associated with ring deformation. Of particular significance, the well-resolved absorption band observed at 420 cm^{-1} provided direct evidence for the formation of Zn-N coordination bonds, confirming the successful coordination between Zn^{2+} ions and imidazole nitrogen atoms and thereby conclusively verifying the assembly of an intact metal–organic framework. The solvothermal temperature primarily governs the nucleation kinetics, with elevated temperatures (e.g., 180 °C) effectively reducing the nucleation energy barrier and promoting the formation of thermodynamically stable crystal nuclei. The reaction duration further affects the growth and morphological evolution of ZIF-8 crystals. A moderate solvothermal duration promotes the formation of highly crystalline ZIF-8 with well-defined hexahedral morphology, whereas excessive growth may lead to particle refinement, compositional changes, and reduced coating compactness. Through systematic optimization of the solvothermal temperature and duration, 180 °C for 24 h was identified as the optimal synthesis condition. Under this condition, ZIF-8 crystals with relatively large grain sizes of 2–6 μm , high crystallinity, and regular hexahedral morphology were obtained, providing effective surface coverage and enhanced barrier protection for the MAO coating.

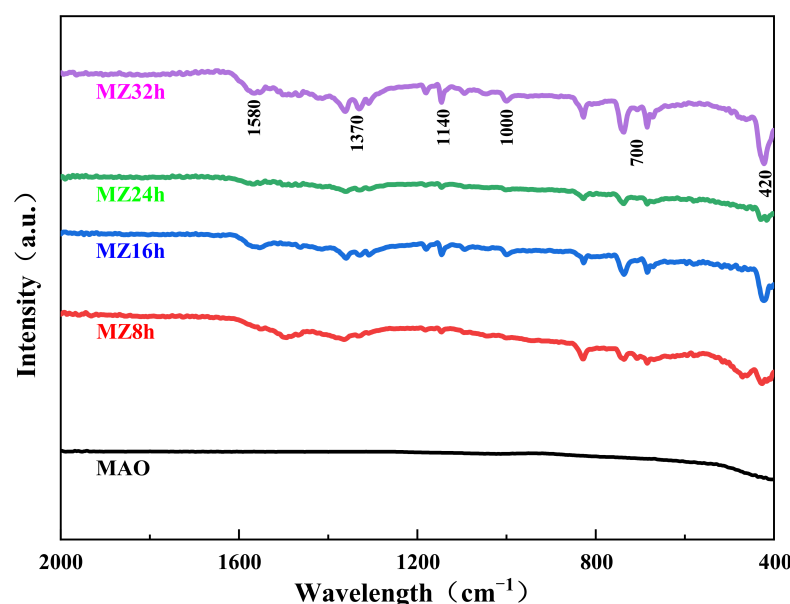


Figure 11. FT-IR spectra of MAO coatings and MAO/ZIF-8 composite coatings prepared at different growth times.

3.2.3. Corrosion Resistance

Polarization curves of MAO and MAO/ZIF-8 coatings at different solvothermal times are shown in Figure 12, while the electrochemical results for MAO/ZIF-8 coatings with

different growth durations are presented in Figure 13. With the extension of solvothermal time, the corrosion resistance of the composite coating first increases and then decreases. Among them, when the growth time is 24 h, the MZ24h coating exhibits the lowest self-corrosion current density ($I_{\text{corr}} = 1.86 \times 10^{-8} \text{ A/cm}^2$), which is one order of magnitude lower than that of the unmodified MAO coating, showing the optimal corrosion resistance performance. The solvothermal reaction time significantly influences the microstructural evolution of the ZIF-8/MAO composite coating and, consequently, its corrosion protection performance. As illustrated in Figures 8–11, the phase composition, surface morphology, and chemical bonding characteristics of the coatings exhibit a clear time-dependent transition, which directly correlates with the electrochemical behavior presented in Figures 12 and 13 and Tables 7 and 8. At an initial stage of 8 h, the coating surface is predominantly composed of dispersed, irregular ZnO nanoparticles with limited ZIF-8 nucleation (Figure 8a,a'). The EDS analysis reveals a high oxygen content (43.0 wt.%) and a relatively low carbon/nitrogen ratio (Table 6), while the XRD pattern shows distinct ZnO diffraction peaks (Figure 10). These features indicate that the ZIF-8 framework remains incomplete. Consequently, the corrosion resistance shows only marginal improvement, with an R_{ct} of $2.60 \times 10^5 \Omega \cdot \text{cm}^2$, which is slightly higher than that of the bare MAO coating ($1.69 \times 10^5 \Omega \cdot \text{cm}^2$). When the reaction time is extended to 16 h, a pronounced phase transformation occurs. The surface morphology evolves into more regular columnar and hexahedral ZIF-8 crystals (Figure 8b,b'), accompanied by a sharp increase in carbon and nitrogen contents (C: 49.1 wt.%, N: 23.1 wt.%) and a significant reduction in oxygen content (23.1 wt.%) (Table 6). The XRD patterns reveal intensified ZIF-8 characteristic peaks, while the FT-IR spectra begin to show imidazole-related vibrational bands, indicating the progressive formation of the ZIF-8 framework. Correspondingly, the R_{ct} increases markedly to $1.02 \times 10^6 \Omega \cdot \text{cm}^2$, and the I_{corr} drops to $6.07 \times 10^{-8} \text{ A} \cdot \text{cm}^{-2}$ (Table 8), reflecting a substantial improvement in barrier performance due to the densification of the ZIF-8 layer and effective sealing of MAO-derived defects. The optimal corrosion resistance is achieved at 24 h. At this stage, the coating exhibits a continuous, well-crystallized ZIF-8 layer composed of large, hexahedral crystals with smooth surfaces (Figure 8c,c'). The EDS analysis shows the lowest oxygen content (19.6 wt.%) and a C/N ratio approaching the theoretical value for ZIF-8 ligands (Table 6). The XRD pattern displays the highest intensity of ZIF-8 diffraction peaks with no detectable ZnO residues (Figure 10), while the FT-IR spectrum confirms the complete formation of Zn-N coordination bonds (Figure 11). These microstructural characteristics translate into the highest R_{ct} of $2.21 \times 10^6 \Omega \cdot \text{cm}^2$ (Table 7) and the lowest I_{corr} of $1.86 \times 10^{-8} \text{ A} \cdot \text{cm}^{-2}$ (Table 8), representing an order-of-magnitude enhancement over the unmodified MAO coating. The dense and defect-free ZIF-8 layer acts as an efficient physical barrier, effectively isolating the underlying metal from corrosive electrolytes. Prolonging the reaction time to 32 h leads to a noticeable degradation in corrosion performance. Although the surface remains fully covered, the ZIF-8 crystals undergo morphological deterioration, transforming into finer, agglomerated structures (Figure 8d,d'). The EDS analysis reveals a slight rebound in oxygen content (23.5 wt.%) and a decrease in carbon and nitrogen levels (Table 6), while the XRD intensity of the ZIF-8 characteristic peak diminishes (Figure 10), suggesting partial framework decomposition or structural reorganization. As a result, the R_{ct} declines to $8.67 \times 10^5 \Omega \cdot \text{cm}^2$ (Table 7), indicating a reduction in barrier performance. This decline may be associated with excessive solvothermal duration, which leads to particle refinement, compositional changes, and reduced coating compactness. Overall, the corrosion resistance of the ZIF-8/MAO composite coating exhibits a non-monotonic dependence on solvothermal time. Extending the reaction time from 8 to 24 h promotes ZIF-8 crystallization, surface defect coverage, and barrier densification, resulting in the optimal protective performance at 24 h. However,

further prolonging the reaction time to 32 h may disturb the coating structure and weaken its barrier integrity, thereby reducing corrosion resistance. These results highlight the importance of precise reaction-time control for fabricating stable and high-performance ZIF-8/MAO composite coatings.

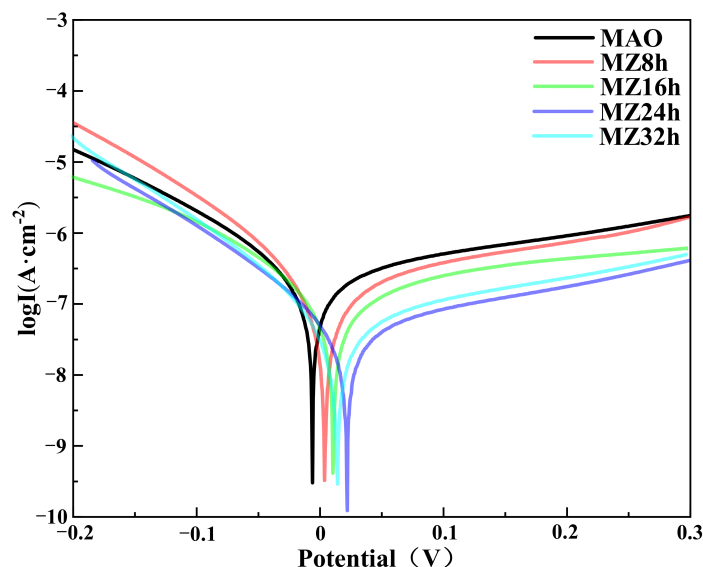


Figure 12. Polarization curves of of MAO coatings and MAO/ZIF-8 coatings prepared at different solvothermal times.

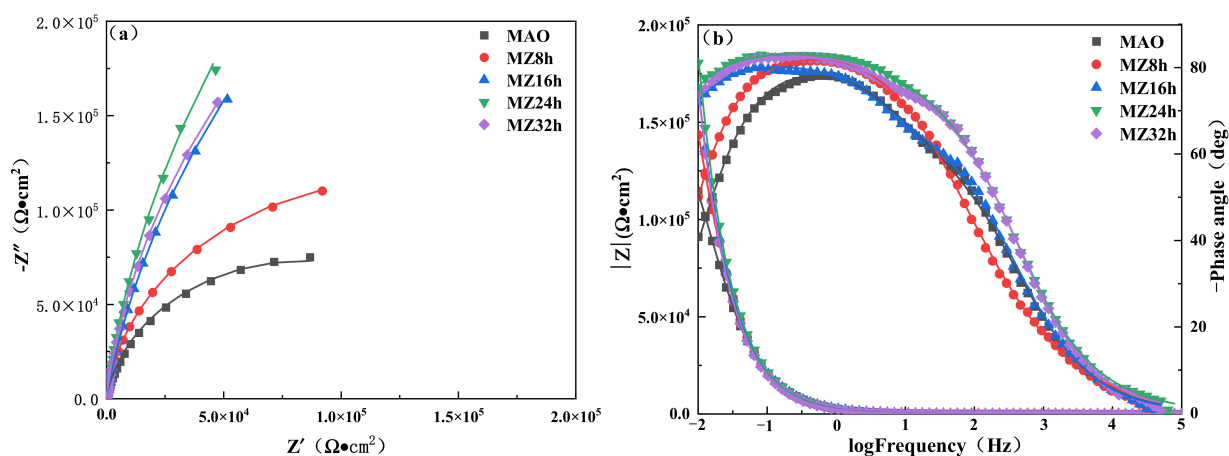


Figure 13. Electrochemical test results of MAO/ZIF-8 composite coatings prepared at different growth times: (a) Nyquist plots; (b) Bode plots.

Table 7. Polarization curve-fitting data of MAO coating and MAO/ZIF-8 composite coating.

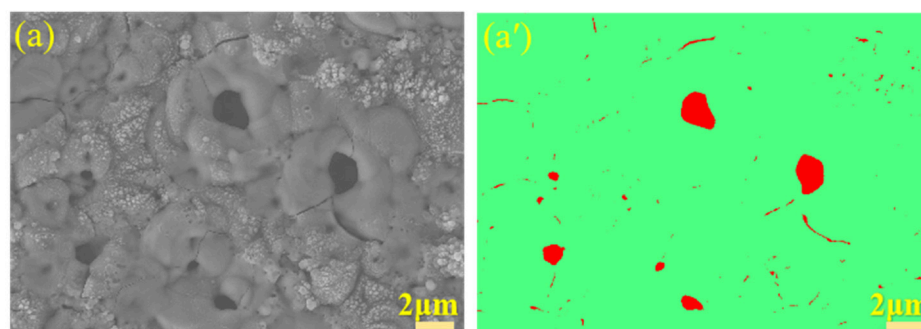
Sample	E_{corr} (V)	I_{corr} (A/cm ²)	CR (mm/y)
MAO	−0.004	1.60×10^{-7}	1.74×10^{-3}
MZ8h	0.001	9.21×10^{-8}	1.00×10^{-3}
MZ16h	0.006	6.07×10^{-8}	6.61×10^{-4}
MZ24h	0.021	1.86×10^{-8}	2.03×10^{-4}
MZ32h	0.013	5.25×10^{-8}	5.72×10^{-4}

Table 8. Fitted data from electrochemical tests of MAO/ZIF-8 composite coatings prepared at different growth times.

Sample	MAO	MZ8h	MZ16h	MZ24h	MZ32h
R_s	11.8	13.5	12.5	11.8	12.6
R_m	183.7	184.8	193.2	198.3	171.2
R_{ct}	1.69×10^5	2.60×10^5	1.02×10^6	2.21×10^6	6.09×10^5

4. Discussion

The inherent porosity of micro-arc oxidation (MAO) coatings—formed by high-voltage micro-arc discharges on metal substrates—generates interconnected discharge channels, resulting in blind and through-pores. When exposed to corrosive media, aggressive agents rapidly infiltrate these pores, reaching the substrate and triggering coating failure with drastically compromised corrosion resistance. The exceptional corrosion resistance of the ZIF-8-modified MAO coating originates from its unique growth mechanism, namely the temperature- and time-controlled in situ growth of ZIF-8 on the micro-arc oxidation coating. The growth mechanism of the MAO/ZIF-8 coating is illustrated in Figure 14.

**Figure 14.** Surface morphology (a) and pore size distribution (a') of MAO coating.

The improved corrosion resistance of the MAO/ZIF-8 composite coatings is mainly associated with the surface coverage and barrier protection provided by the controlled in situ solvothermal growth of ZIF-8 on the MAO coating. Compared with the conventional synthesis of free-standing ZIF-8 particles or films, the present strategy uses the microporous ceramic MAO layer as a surface scaffold for ZIF-8 growth. The MAO coating, with its characteristic volcano-like morphology, abundant micropores, and microcracks (Figure 14), provides a textured surface with numerous sites favorable for heterogeneous nucleation and particle anchoring. In addition, the porous MAO surface may influence the local growth environment during solvothermal treatment, which facilitates the formation of ZIF-8-containing coatings on the MAO surface. Solvothermal temperature plays an important role in regulating the phase composition and morphology of the surface products. At lower temperatures (100–140 °C), the reaction conditions may be insufficient to promote effective coordination between Zn^{2+} ions and 2-methylimidazole ligands. As a result, ZnO-related products are mainly observed on the MAO surface (Figure 1b,c). This is supported by the EDS results showing relatively high Zn and O contents with low C and N contents (Table 3), the XRD detection of ZnO peaks, and the absence or weakness of characteristic Zn–N vibration signals in the FT-IR spectra. Such ZnO-rich and relatively loose surface products provide only limited improvement in corrosion protection. At 180 °C, a clear change in coating composition and structure is observed. The increased solvothermal temperature promotes the formation of ZIF-8-containing structures, as indicated by the enhanced C and N signals, the appearance of characteristic ZIF-8 diffraction peaks, and the Zn–N-related vibration in the FT-IR spectra. These results suggest a transition from ZnO-rich products to

ZIF-8-rich surface structures, which improves surface coverage and barrier protection of the MAO coating. SEM observations show the coexistence of ZnO-related particles and newly formed ZIF-8 crystals at this stage (Figure 1d). This transition is further supported by the EDS results, which show a pronounced increase in C and N contents together with a sharp decrease in the Zn signal. The resulting coating forms a relatively continuous ZIF-8 layer that helps seal the defects in the underlying MAO coating, thereby contributing to the improved corrosion resistance observed in both EIS and polarization tests. At 220 °C, although the SEM morphology shows uniform and highly crystalline ZIF-8 crystals (Figure 1e), EDS analysis reveals a relatively high Zn content together with a detectable oxygen signal. These compositional features may be associated with incomplete conversion of ZnO precursors, oxygen-containing species, or local structural imperfections induced by excessive solvothermal temperature. Such changes may weaken the barrier performance of the composite coating, suggesting that higher crystallinity does not necessarily lead to optimal corrosion protection.

As Figure 1 illustrates, elevated solvothermal temperatures overcome coordination reaction activation barriers, accelerating ZIF-8 nucleation while enabling crystallographically oriented growth via Ostwald ripening. Enhanced coordination kinetics and ripening effects drive in situ ZIF-8 crystallization across MAO surfaces. During solvothermal progression (8→32 h), ZIF-8 crystals evolve through the following distinct morphological stages: ① nucleation—irregular nanoparticles; ② directional growth—axially aligned columnar structures; ③ multidimensional assembly—laterally branched architectures; and ④ maturation—low-surface-energy 3D hierarchical clusters.

This transition from axial extension to ripening-dominated hierarchical assembly culminates in compact, surface-energy-minimized architecture. Critically, ZIF-8 grows in situ across MAO surfaces and within micropores, simultaneously sealing porosity defects and establishing a dense diffusion barrier against corrosive infiltration.

The growth of ZnO@ZIF-8 proceeds through three distinct stages:

- (1) Early Stage (8~16 h):
 - ①. Crystals primarily undergo nucleation and unidirectional growth, gradually forming columnar- or rod-like morphologies.
 - ②. The morphology transitions from irregular particles to regular columnar structures.
- (2) Intermediate Stage (16~24 h):
 - ①. Columnar crystals further develop, with significant increases in crystal size, and some crystals begin to exhibit lateral growth tendencies.
 - ②. Columnar growth approaches saturation, and surface porosity progressively decreases.
- (3) Late Stage (24~32 h):
 - ①. Crystal size continues to expand, accompanied by pronounced lateral growth and secondary nucleation, ultimately forming complex flower-like or clustered morphologies.
 - ②. The morphological complexity likely arises from reduced zinc ion concentration in the solution, promoting Ostwald ripening and multidirectional crystal growth.

The main feature of this strategy is the controlled in situ growth of ZIF-8 on the surface of the MAO ceramic layer by adjusting the solvothermal temperature and duration. The porous MAO coating provides a textured surface that is favorable for the nucleation and anchoring of ZIF-8-containing products. Based on the SEM, EDS, XRD, and FT-IR results, the coating evolution can be described as a transition from ZnO-rich surface products to ZIF-8-rich structures under appropriate solvothermal conditions. The solvothermal temperature mainly affects the formation of the ZIF-8 phase, whereas the reaction time influences crystal growth, surface coverage, and coating compactness.

This in situ growth approach improves the surface coverage of the MAO coating and contributes to the reduction in exposed micropores and cracks, thereby enhancing the barrier protection of the composite coating. The coating synthesized at 180 °C for 24 h exhibits a favorable combination of ZIF-8 formation, high crystallinity, relatively dense morphology, and improved corrosion resistance. As a result, its charge transfer resistance is more than one order of magnitude higher than that of the bare MAO coating.

5. Conclusions

The MAO/ZIF-8 composite coatings were successfully fabricated on micro-arc-oxidized aluminum alloy substrates via in situ solvothermal growth. The formation of ZIF-8-containing surface layers was confirmed by SEM, EDS, XRD, and FT-IR analyses. The grown ZIF-8 particles covered the MAO surface and contributed to the sealing of surface micropores and cracks, thereby improving the barrier protection of the coating. The corrosion resistance of the composite coatings was strongly dependent on the solvothermal temperature and duration, with appropriate growth conditions leading to enhanced coating compactness and electrochemical performance. The key findings are summarized as follows:

- (1) ZIF-8/MAO composite coatings were successfully prepared on micro-arc-oxidized aluminum alloy substrates via in situ solvothermal growth. The solvothermal temperature and duration significantly affected the phase composition, surface morphology, and elemental distribution of the coatings. Appropriate growth conditions promoted the formation of ZIF-8-containing surface layers, while an excessive temperature or prolonged reaction time led to unfavorable morphological and compositional changes.
- (2) The improved corrosion resistance of the composite coating was mainly associated with the enhanced surface coverage and barrier protection provided by the in situ-grown ZIF-8 particles. The ZIF-8-containing layer reduced the exposure of surface micropores and cracks in the MAO coating, thereby inhibiting electrolyte penetration and improving the protective performance. The unsupported statement regarding auxiliary chemical self-healing has been removed.
- (3) The coating prepared at 180 °C for 24 h exhibited the best overall corrosion resistance. Its charge transfer resistance reached $2.21 \times 10^6 \Omega \cdot \text{cm}^2$, which is more than one order of magnitude higher than that of the unmodified MAO coating, while its corrosion rate was minimized. These results demonstrate that proper control of the solvothermal temperature and duration is essential for obtaining ZIF-8/MAO composite coatings with enhanced barrier protection.

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Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

MAO	Micro-Arc Oxidation
ZIF-8	Zeolitic Imidazolate Framework-8
LDH	Layered Double Hydroxide
C ₄ H ₆ N ₂	2-methylimidazole
CR	Corrosion rate

References

1. Au Chen, Q.; Jiang, Z.; Tang, S.; Dong, W.; Tong, Q.; Li, W. Influence of graphene particles on the micro-arc oxidation behaviors of 6063 aluminum alloy and the coating properties. *Appl. Surf. Sci.* **2017**, *423*, 939–950. [\[CrossRef\]](#)
2. Liu, X.D.; Wang, C.X.; Lei, J.L.; Song, P.; Huang, T.H.; Zhang, X.W.; Yang, T.F.; Ji, V. Micro-Arc Oxidation of Aluminum Alloys: Mechanism, Defects, and Corrosion Resistance. *Adv. Eng. Mater.* **2025**, *27*, 2402748. [\[CrossRef\]](#)
3. Yao, Y.F.; Yi, Z.C.; Chong, W.J.; Li, K.Y.; Huang, Q.L.; Liu, Y.; Wen, C.; Wu, H. Micro-arc oxidation surface-modification of titanium alloys for biomedical applications: Mechanisms, advances, challenges, and prospects. *Prog. Mater. Sci.* **2026**, *159*, 101654. [\[CrossRef\]](#)
4. Zhao, C.; Wang, X.W.; Li, C.P.; Liu, Y.; Sun, S.; Yang, S.S.; Sun, Y.C.; Peng, Z.J.; Yu, Q.L.; Cai, M.R. Superior tribological and anti-corrosion performance of corrosion inhibitors intercalated LDH-MAO coating on AZ31 Mg alloys. *Tribol. Int.* **2024**, *191*, 109126. [\[CrossRef\]](#)
5. Amin, A.; Awad, I.; Ibrahim, H. Corrosion prediction for MAO-coated magnesium using machine learning approach. *Mater. Today Commun.* **2026**, *50*, 114471. [\[CrossRef\]](#)
6. Malayoglu, U.; Tekin, K.C.; Shrestha, S. Influence of post-treatment on the corrosion resistance of PEO coated AM50B and AM60B Mg alloys. *Surf. Coat. Technol.* **2010**, *205*, 1793–1798. [\[CrossRef\]](#)
7. Kiani, M.; Javidi, M. ZIF-8 nanoparticles synthesis for pH-sensitive release of corrosion inhibitor. *J. Solid State Chem.* **2024**, *338*, 124849. [\[CrossRef\]](#)
8. Wang, Y.; Yin, H.R.; He, X.Y.; Zhou, D.; Zhang, B.; Bai, X.X.; Mao, R.B.; Chu, F.N.; Zhang, W.W. ZIF-8@SCC/AgNW nanocone coatings on Mg alloys for synergistic corrosion resistance and photodynamic antibacterial. *Mater. Des.* **2025**, *260*, 115189. [\[CrossRef\]](#)
9. Wu, Y.C.; Wang, Y.; Liu, J.Y.; Wu, J.; Liu, Y.C. In situ engineered layered ZIF-8@ZnAl-LDO hybrids for high-capacity chloride adsorption and synergistic corrosion protection. *Colloid Surf. A* **2026**, *728*, 138520. [\[CrossRef\]](#)
10. Chen, K.X.; Yang, X.Q.; Qu, Q.; Wu, T.; Chen, S.; Li, L. Inhibition of microbiologically influenced corrosion and biofouling of X70 carbon steels by near-superhydrophobic D-cysteine/Ag@ZIF-8 coatings. *Corros. Sci.* **2022**, *208*, 110682. [\[CrossRef\]](#)
11. Ma, X.X.; Li, Y.H.; Huang, A.S. Synthesis of nano-sheets seeds for secondary growth of highly hydrogen permselective ZIF-95 membranes. *J. Membr. Sci.* **2020**, *597*, 117629. [\[CrossRef\]](#)
12. Yoo, Y.; Jeong, H.K. Rapid fabrication of metal organic framework thin films using microwave-induced thermal deposition. *Chem. Commun.* **2008**, *21*, 2441–2443. [\[CrossRef\]](#)
13. Yoo, Y.; Lai, Z.P.; Jeong, H.K. Fabrication of MOF-5 membranes using microwave-induced rapid seeding and solvothermal secondary growth. *Microporous Mesoporous Mater.* **2009**, *123*, 100–106. [\[CrossRef\]](#)
14. Reif, B.; Somboonvong, J.; Fabisch, F.; Kaspereit, M.; Hartmann, M.; Schwieger, W. Solvent-free transformation of spray coated ZnO layers to ZIF-8 membranes. *Microporous Mesoporous Mater.* **2019**, *276*, 29–40. [\[CrossRef\]](#)
15. Jin, S.Y.; Zhou, J.; Wu, R.Z.; Ma, X.C.; Yu, Z.; Wang, G.X.; Zhang, J.H.; Krit, B.; Betsofen, S.; Vitalii, N.; et al. In-situ growth of corrosion-resistant LDH/ZIF-8 hybrid film on the surface of MAO film based on LA93 alloy by the one-step method. *Appl. Surf. Sci.* **2024**, *671*, 160742. [\[CrossRef\]](#)
16. Jiang, S.Q.; Zhang, Z.Y.; Wang, D.; Wen, Y.Q.; Peng, N.; Shang, W. ZIF-8-based micro-arc oxidation composite coatings enhanced the corrosion resistance and superhydrophobicity of a Mg alloy. *J. Magnes. Alloys* **2023**, *11*, 1367–1380. [\[CrossRef\]](#)
17. Cui, L.Y.; Zeng, R.C.; Guan, S.K.; Qi, W.C.; Zhang, F.; Li, S.Q.; Han, E.H. Degradation mechanism of micro-arc oxidation coatings on biodegradable Mg-Ca alloys: The influence of porosity. *J. Alloys Compd.* **2017**, *695*, 2464–2476. [\[CrossRef\]](#)
18. Sedelnikova, M.B.; Mayer, V.V.; Bakina, O.V.; Kashin, A.D.; Uvarin, P.V.; Khimich, M.A.; Luginin, N.A.; Glukhov, I.A.; Tolkacheva, T.V.; Ugodchikova, A.V.; et al. Antibacterial Amorphous–Crystalline Coatings Based on Wollastonite and ZnO Particles. *Crystals* **2024**, *14*, 886. [\[CrossRef\]](#)
19. Asghar, M.S.A.; Hussain, U.; Ovais, M.; Khan, S.A.; Aabid, A.; Baig, M.; Malik, M.A. Development of corrosion-resistant hydrophobic Zn/ZnO composite coatings on steel substrates. *Mater. Res. Express* **2025**, *12*, 026401. [\[CrossRef\]](#)

20. Kania, A.; Szindler, M.M.; Szindler, M.; Brytan, Z.; Kciuk, M.; Pakiela, W.; Reimann, L.; Nuckowski, P.M. ZnO Thin Films as Promising Corrosion Protection on Mg-Based Alloys. *Materials* **2025**, *18*, 5568. [[CrossRef](#)] [[PubMed](#)]
21. Zeng, Y.W.; Xu, P.; Liu, G.Q.; Wang, T.G.; Lei, B.; Feng, Z.Y.; Zhang, P.; Meng, G.Z. ZIF-8 Modified Ce-Sol-gel Film on Rebar for Enhancing Corrosion Resistance. *Acta Metall. Sin. (Engl. Lett.)* **2024**, *37*, 2121–2135. [[CrossRef](#)]
22. Wu, L.; Ye, Q.Y.; Zhang, K.; Guo, X.Y.; Li, J.Q.; Chen, Y.N.; Fang, F.; Chang, H.T. Fabrication of hydrophobic corrosion-resistant microarc oxidation titanium alloy through pore-sealing treatment with secondary growth of ZIF-8 seed crystals. *Surf. Coat. Technol.* **2025**, *501*, 131898. [[CrossRef](#)]
23. Liu, X.Z.; Li, L.X.; Wang, M.; Zhang, B.B. Robust ZIF-8 based superhydrophobic coating with anti-icing, anti-corrosion, and substrate universality. *J. Ind. Eng. Chem.* **2025**, *144*, 679–690. [[CrossRef](#)]
24. Zhang, W.Y.; Zhang, X.W.; Zhang, T.; Meng, Q.K.; Sui, Y.W.; Wei, F.X.; Xiao, B.; Zhang, C.J.; Qi, J.Q. Investigation on the Augmentation of Corrosion Resistance in Zn-Al Coating via ZIF-8 Hydrophobic Films. *J. Mater. Eng. Perform.* **2026**, *35*, 46–56.
25. Chen, Y.T.; Tang, S.K. Solvothermal synthesis of porous hydrangea-like zeolitic imidazole framework-8 (ZIF-8) crystals. *J. Solid State Chem.* **2019**, *276*, 68–74. [[CrossRef](#)]
26. Zhang, W.Y.; Zhang, T.; Zhang, X.W.; Qi, J.Q.; Ni, Y.; Wei, F.X.; Sui, Y.W.; Meng, Q.K.; Kang, Z.S.; Zhu, L. Investigation of enhanced corrosion resistance in Zn-Al coating via novel ZIF-8/LDH composite films. *Anti-Corros. Methods Mater.* **2025**, *72*, 672–680. [[CrossRef](#)]
27. Tsuruoka, T.; Araki, K.; Kawauchi, K.; Takashima, Y.; Akamatsu, K. Direct Formation of ZIF-8 Crystal Thin Films on the Surface of a Zinc Ion-Doped Polymer Substrate. *Inorganics* **2024**, *12*, 21. [[CrossRef](#)]
28. Wang, H.D.; Liu, J.; Liu, B.S.; Zhang, Z.C.; Ren, X.X.; Wang, X.T.; Wu, P.P.; Zhang, Y.Z. Direct In Situ Fabrication of Strong Bonding ZIF-8 Film on Zinc Substrate and Its Formation Mechanism. *Metals* **2024**, *14*, 1403. [[CrossRef](#)]
29. Sharma, R.; Van Assche, T.R.C.; Baron, G.V.; Denayer, J.F.M. Copper-induced synthesis of zinc imidazolate metal-organic framework (ZIF-8) crystals and coatings. *Microporous Mesoporous Mater.* **2022**, *343*, 112163. [[CrossRef](#)]
30. Kasneryk, V.; Gazenbiller, E.; Wieland, D.C.F.; Garamus, V.M.; Serdechnova, M.; Blawert, C.; Zheludkevich, M.L. From Zn-Al LDH to ZIF-8@Zn-Al LDH conversion coatings on the surface of AA2024 alloy: Inside the process and the effect of the transformation on the protective properties. *Surf. Interfaces* **2025**, *59*, 105958. [[CrossRef](#)]
31. Chavhan, J.; Prabhakar, M.; Ganapathi, A.; Rohwerder, M.; Neelakantan, L. Multifunctional Epoxy/PVDF smart coatings using ZIF-8 nanosensor for corrosion protection of mild steel: A study on synthesis and performance. *Prog. Org. Coat.* **2025**, *203*, 109198. [[CrossRef](#)]
32. Wang, C.Y.; Wang, J.H.; Hu, W.B. Preparation and corrosion resistance of ZnO@ZIF-8-SA film on carbon steel surface. *Colloid Surf. A* **2022**, *647*, 129017. [[CrossRef](#)]
33. Zhang, H.; Zhao, M.; Yang, Y.; Lin, Y.S. Hydrolysis and condensation of ZIF-8 in water. *Microporous Mesoporous Mater.* **2019**, *288*, 109568. [[CrossRef](#)]

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