Fabrication and Corrosion Resistance of a Superhydrophobic Ni–P/Ni₃(NO₃)₂(OH)₄ Multilayer Protective Coating on Magnesium Alloy

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ABSTRACT: A superhydrophobic multilayer coating with excellent corrosion resistance has been fabricated on an AZ61 magnesium alloy through electroless plating and hydrothermal treatment. The surface morphologies, chemical characteristics, wettabilities, and corrosion resistance of the multilayer coating were characterized and discussed. The results show that the electroless Ni–P coating on the magnesium alloy exhibits a nodular structure with micropores and lower corrosion resistance. However, a dense Ni₃(NO₃)₂(OH)₄ layer, a porous Ni₃(NO₃)₂(OH)₄ nanostructure layer, and a stearic absorbing layer are grown on the surface of the Ni–P coating with superhydrophobic characters and higher corrosion resistance after hydrothermal treatment. Furthermore, the water contact angle and corrosion resistance of the multilayer coating showed a trend of first increasing and then decreasing as the hydrothermal reaction time increases. The optimum hydrothermal reaction time is 15 h, and the multilayer coating prepared under this condition has the highest corrosion resistance and the highest contact angle. In addition, the protection mechanism of the multilayer coating is discussed, and the formation of the dense Ni₃(NO₃)₂(OH)₄ layer and the stearic absorbing layer effectively improved the corrosion resistance of the multilayer coating.

1. INTRODUCTION

It is well known that electroless plating of Ni–P coating is a preferred way to enhance the corrosion resistance of magnesium alloy pieces of irregular shapes because of simple operation, high efficiency, and low cost.¹–³ However, the β phase (Mg₁₇Al₁₂ intermetallic) on the surface of an AZ61 magnesium alloy is more cathodic than the eutectic α and primary α phases, leading to nonuniform coating growth and coating porosity.⁴,⁵ Since the electroless Ni–P coating on the magnesium alloy substrate is a cathodic coating, the caustic ions in the solution can easily reach the substrate through these pores, triggering galvanic corrosion between the Ni–P coating and the substrate, resulting in an evident decrease in corrosion protection.⁶ Hence, a single electroless Ni–P coating is inappropriate for a general industrial use directly.

Recently, bilayer coatings, such as chemical conversion coating/electroless coating and microarc oxidation (MAO)/electroless coating, are proposed to improve the corrosion resistance of the traditional single Ni–P coating.⁷–¹² Seifzadeh et al. investigated the electroless Ni–P coating on magnesium alloy treated by a cerium–lanthanum–permanganate (CLP) conversion coating,⁷ a titane conversion coating,⁸ and a strontium phosphate conversion coating.⁹ Singh et al. prepared a carbonate and phosphate conversion pretreatment with two steps before the electroless nickel coating.¹⁰ Fan et al. designed an MAO coat as the intermediate layer for the electroless-plated Ni–P topcoat, and the composite coat has excellent corrosion resistance and a stable bonding interface.¹¹ Ezhilselvi et al. developed an MAO coating as the interlayer for the electroless Ni–P top coating, and the duplex coating showed about two orders of improved corrosion resistance than the substrate due to the pore-free dense uniform Ni–P coating developed over the MAO interlayer.¹² Superhydrophobic films have been proven to be an effective method for protecting magnesium alloy from corrosion as an
air cushion created by the superhydrophobic structure could inhibit the migration of corrosion ions.\textsuperscript{13,14} However, the corrosion resistance of a single superhydrophobic film is unsatisfactory due to its loose structure and limited thickness.\textsuperscript{15−17} By combining the superhydrophobic topcoat and the bottom plating, such as MAO coating, electroplating, and conversion coating, the corrosion resistance of the magnesium (Mg) alloy has improved a lot.\textsuperscript{18−20} For example, Cui et al. fabricated a hydrophobic surface on the top of MAO coating, and the hydrophobic MAO coating effectively inhibited corrosion of the Mg alloy, especially pitting corrosion.\textsuperscript{18} Liu et al. prepared a superhydrophilic topcoat after electroplating Ni, and the result shows that the as-prepared superhydrophobic film-deposited surface could effectively protect the substrate from corrosion.\textsuperscript{19} Zhang et al. fabricated a superhydrophobic calcium phosphate chemical conversion coating with remarkable anticorrosion properties.\textsuperscript{20} Furthermore, using a hydrothermal process, some special nanostructures or a micro-/nanohierarchical structure can be easily obtained, and the superhydrophobic surface can be fabricated on the micro-/nanohierarchical structure with the help of materials with a low surface free energy.\textsuperscript{21} In addition to superhydrophobicity, hydrothermal treatment is a good way to repair micropores and defects on a substrate because it shows preferred nucleation in the cracks and defects of the substrate.\textsuperscript{22,23}

In this paper, an electroless Ni−P coating was prepared on the AZ61 magnesium alloy at first, and then hydrothermal treatment was carried out on the electroless Ni−P coating to obtain a superhydrophobic multilayer coating. The surface morphologies, chemical compositions, structures, and wettability of the multilayer coating were characterized and determined, and the corrosion resistance of the coating was measured by electrochemical techniques. Furthermore, the protection mechanism of the multilayer coating is discussed, and the hydrothermal reaction time was optimized.

2. RESULTS

2.1. Surface Morphology. Figure 1 shows SEM images of the electroless Ni−P coating before and after hydrothermal post-treatment. After electroless plating, the surface of the substrate is covered with a large amount of nodular structures of different nodule sizes (Figure 1a), and several small pores are randomly distributed on the surface of coating (Figure 1b). These pores are relevant to the release of hydrogen during plating and are hard to avoid.\textsuperscript{24} However, a lot of nanosheets grow vertically on the surface of the Ni−P coating, and some locations appear like 3D flowerlike nanoclusters after the hydrothermal reaction (Figure 1c,d). The pores and defects on the surface of the Ni−P coating are repaired by the growth of nanosheets because these positions are preferentially nucleation sites during the hydrothermal reaction due to a higher surface energy than other locations.\textsuperscript{22,23}

Figure 2 shows the morphological evolution of the nanosheets at different hydrothermal reaction times. A two-level hierarchical nanostructure is formed gradually, and the size of the 3D nanoclusters increases with reaction time. Only a few flowerlike 3D nanoclusters can be observed when the reaction time is 9 h, but they grow on a large scale after 12 h. The two-level hierarchical nanostructure consists of an inner layer, that is, vertically aligned nanosheet arrays and an outer layer, that is, 3D nanoclusters that have fully formed when the reaction time is 15 h as the 3D nanoclusters covered the whole surface at that time. The size of the nanoclusters further increases to several micrometers when the reaction time increases up to 18 h.

2.2. Thickness. Figure 3 shows the thickness of the nanostructure layer after different hydrothermal reaction times.

Figure 3 shows the thickness of the Ni−P coating after post-treatment with different hydrothermal reaction times: (a) 9 h, (b) 12 h, (c) 15 h, and (d) 18 h.

The layer becomes gradually thicker with increasing reaction time, and the average thickness of the nanostructure layer is 3.4 μm (9 h), 4.5 μm (12 h), 5.4 μm (15 h), and 5.8 μm (18 h), respectively. On the whole, the nanostructure layers consist of a compact inner layer and a loose outer layer except for the hydrothermal time of 9 h, and the thickness of the inner layer increases with the hydrothermal reaction time increasing from 12 to 18 h. There is a clear dividing line between the Ni−P
coating and the nanostructure layer when the reaction time is 9 h. Both transverse and vertical cracks are distributed in the nanostructure layer prepared with a reaction time of 18 h, but the vertical cracks do not run through the entire layer.

### 2.3. Structure and Chemical Composition.

X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) are used to study the structure and the chemical composition of the Ni–P coating after a hydrothermal treatment of 15 h (Ni–P-T-15 h). Figure 4 shows the XRD patterns of Ni–P coating and Ni–P-T-15 h coating. In the XRD pattern of the Ni–P coating, only one broadened diffraction peak of the Ni phase at 44.5° is detected, which indicates that the Ni–P coating is in an amorphous state. In the XRD pattern of the Ni–P-T-15 coating, except for the peak of the Ni phase, the rest of the diffraction peaks at 13, 26, 36, and 59° can be indexed to the (001), (002), (101), and (110) planes of the hexagonal structure of Ni(NO$_3$)$_2$(OH)$_4$ (JCPDS NO: 22-0752). The generation of Ni(NO$_3$)$_2$(OH)$_4$ is expressed as follows:

$$3\text{Ni(NO}_3\text{)}_2 + 4\text{H}_2\text{O} \rightarrow \text{Ni}_3\text{(NO}_3\text{)}_2(\text{OH})_4 + 4\text{HNO}_3$$

(1)

The result suggests that the chemical composition of the nanosheets and nanoclusters formed on the surface of the Ni–P coating during the hydrothermal reaction is Ni(NO$_3$)$_2$(OH)$_4$ which is derived from a metal hydroxide and has a layered CdI$_2$ structure.

Figure 5 shows the FT-IR spectra of pure stearic acid and Ni–P-T-15 coating. For the stearic acid, the peaks at 2844 and 2923 cm$^{-1}$ are attributed to the C–H asymmetric and symmetric stretching vibrations, and the peak at 1705 cm$^{-1}$ is assigned to the carboxyl (–COOH) group of stearic acid.

For the Ni–P-T-15 coating, the FT-IR spectra reveal the existence of –OH stretching vibrations (~3641 cm$^{-1}$), NO$_3^-$ vibrations (~1386 cm$^{-1}$), δ(OH) of hydroxyl group (~640 cm$^{-1}$), Ni–O vibrations, and Ni–O–H bending vibrations (~486 cm$^{-1}$), which are functional groups of Ni(NO$_3$)$_2$(OH)$_4$ and the adsorption peaks at 2862 cm$^{-1}$ and 2930 cm$^{-1}$ are attributed to the –CH$_3$ or –CH$_2$ functional group, but the –COOH absorption peak disappear. However, a new absorption peak arises at 1497 cm$^{-1}$, which stems from the stretching vibration of the –COO– groups. All these results indicate that the surface of the multilayer coating has a low surface energy probably because of the formation of Ni(CH$_3$(CH$_2$)$_{16}$COO)$_2$.

Figure 6 shows the XPS spectra of the Ni–P-T-15 h coating. In the survey spectrum (Figure 6a), C 1s, O 1s, Ni 2p, and Ni 1s are detected. The C 1s spectrum consists of three peaks; the peaks at 284.7 and 285.4 eV are attributed to –CH$_3$ and –CH$_2$–, respectively, and the peak at 288.2 eV is attributed to the –COOH bond (Figure 6b). The O 1s spectrum reveals the presence of three peaks located at 530.9, 531.5, and 532.7 eV. The peak at 530.9 originates from the Ni–OH binding, and the peaks at 531.5 and 532.7 are assigned to the C=O and C–O– bonds, respectively (Figure 6c). The Ni 2p spectrum consists of 2p$_{3/2}$ and 3p$_{3/2}$, the peak at 879.8 eV and its satellite at 873.5 eV are assigned to Ni$^{2+}$ (3p$_{3/2}$), and the peak at 855.7 eV and its satellite at 861.7 eV are assigned to Ni$^{3+}$ (3p$_{3/2}$) (Figure 6d).

Based on the XRD, FT-IR, and XPS results, we can deduce that the surface of the Ni–P-T-15 h coating mainly consists of a Ni$_3$(NO$_3$)$_2$(OH)$_4$ nanostructure and Ni(CH$_3$(CH$_2$)$_{16}$COO)$_2$ with a low surface energy.

### 2.4. Wettability and Chemical Stability.

The surface of the multilayer coating exhibits superhydrophobic benefits from the formation of a two-level hierarchical nanostructure and modification by a low surface energy substance stearic acid. The variation of water contact angle and sliding angle of the superhydrophobic film with hydrothermal reaction time is shown in Figure 7. The contact angle first increases and then decreases with reaction time, and the changing trend of the sliding angle is seen in an opposite direction. At 9 h, the contact angle and the sliding angle reached 153.5 and 3°. When the reaction time is increased to 12 h, the contact angle remained unchanged, but the sliding angle reduced to 2°. Furthermore, the contact angle reaches a maximum value of 156.5° and the corresponding sliding angle reaches a minimum value of 2° after 15 h. However, the contact angle returned to 150.8° and the sliding angle increased to 10° when the reaction time was extended to 18 h.

Figure 8 shows the relationship between the contact angle and pH values of the liquid droplets for the Ni–P-T coatings at different hydrothermal reaction times. The contact angle of all coatings is greater than 140° when the pH values change from 1 to 14. The contact angle of Ni–P-T-9 h is 142°, while that of Ni–P–T-15 h is 150° when they are in contact with a solution with a pH of 1. At the same time, when they are in contact with a solution with a pH of 14, the contact angle of Ni–P-T-9 h is 140°, while that of Ni–P–T-15 h is 148°. Therefore, the chemical stability of Ni–P–T-15 h is better than that of Ni–P–T-9 h.

### 2.5. Corrosion Resistance.

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) are used to study the corrosion behavior of the AZ61 substrate, Ni–P coating, and Ni–P coating after hydrothermal treatment at...
different times (Ni–P-T-9 h, Ni–P-T-12 h, Ni–P-T-15 h, and Ni–P-T-18 h).

2.5.1. Potentiodynamic Polarization Curves. Figure 9 shows the potentiodynamic polarization curves of the substrate, Ni–P coating, and Ni–P–T coatings in 3.5% NaCl. The corrosion potential ($E_{\text{corr}}$), corrosion current density ($i_{\text{corr}}$), and inhibition efficiency $\eta_1$ ($\eta_1 = \left(\frac{i_{\text{corr}}}{i_{\text{corr}}}\right)_{\text{substrate}}$) are shown in Table 1. The lower $i_{\text{corr}}$ and the higher $\eta_1$ reflect the lower corrosion rate and better corrosion resistance. The value of $i_{\text{corr}}$ reduces a lot, and $\eta_1$ increases a lot for Ni–P–T coatings compared with the AZ61 substrate and Ni–P coating. Furthermore, $i_{\text{corr}}$ for Ni–P–T coatings decreases first and then increases with the increase in hydrothermal reaction time, while the value of $\eta_1$ shows the opposite trend. The Ni–P–T-15 h coating exhibits the lowest $i_{\text{corr}}$ ($1.1 \times 10^{-2} \mu A/cm^2$), which dropped four orders of magnitude.

| sample         | $E_{\text{corr}}$ (mV) | $i_{\text{corr}}$ ($\mu A/cm^2$) | $\eta_1$ (%) |
|----------------|------------------------|----------------------------------|--------------|
| AZ61 substrate | -1548.0                | 35.3                             | 76.49        |
| Ni–P           | -656.7                 | 8.3                              | 94.90        |
| Ni–P-9 h       | -331.3                 | 1.8                              | 99.86        |
| Ni–P-12 h      | -139.2                 | $4.9 \times 10^{-2}$             | 99.97        |
| Ni–P-15 h      | -283.7                 | $1.1 \times 10^{-2}$             | 99.97        |
| Ni–P-18 h      | -154.3                 | $3.2 \times 10^{-2}$             | 99.91        |

Table 1. Corrosion Potential, Current Density, and Polarization Resistance of the AZ61 Substrate, Ni–P Coating, and Ni–P–T Coatings in 3.5% NaCl Solution from the Polarization Curve.
magnitude efficiency than the AZ61 substrate, and the corrosion inhibition efficiency reaches 99.99%. This result suggests that the Ni−P-T-15 h coating can effectively protect the substrate, and the electron transfer ability in the electrolyte is strongly suppressed by the outer superhydrophobic film and the inner Ni−P coating.

2.5.2. Electrochemical Impedance Spectroscopy. Figure 10 shows the EIS spectra of the AZ61 substrate, Ni−P coating, and Ni−P-T coatings in 3.5% NaCl solution. In the EIS spectrum of the AZ61 substrate, there are two capacitive loops found (Figure 10a,d) in which the capacitance loop at a higher frequency is a result of capacitance CPEfilm and resistance $R_{film}$ of the oxide or hydroxide layer on the AZ61 substrate, and the capacitance loop at a lower frequency is a result of the double-layer capacitance CPE_{dl} and charge transfer resistance $R_{ct}$ of the AZ61 substrate. In the EIS spectrum of Ni−P coating, there are also two capacitive loops found (Figure 10a,d) in which the capacitance loop at a higher frequency is a result of capacitance CPEfilm and resistance $R_{film}$ of the Ni−P coating on the AZ61 substrate, and the capacitance loop at a lower frequency is a result of double-layer capacitance CPE_{dl} and charge transfer resistance $R_{ct}$ of the AZ61 substrate. In the EIS spectrum of Ni−P-T coatings, three capacitive loops could be observed in which two capacitance loops at higher frequencies originate from CPE_{super} and $R_{super}$ of the superhydrophobic layer, and CPE_{film} and $R_{film}$ of the hydrothermal oxide layer and Ni−P layer, while the capacitance loop at a lower frequency is the double-layer capacitance CPE_{dl} and the charge transfer resistance $R_{ct}$ of the AZ61 substrate. Furthermore, the capacitive diameter of the Ni−P-T coating ($10^3 \sim 10^7 \Omega \cdot cm^2$) is much larger than that of the AZ61 substrate and Ni−P coating, which implies that the corrosion resistance of the AZ61 alloy is greatly improved after hydrothermal treatment. With the hydrothermal reaction time increasing, the capacitive diameter of the Ni−P-T coating first increases and then decreases, and the Ni−P−T coating with a reaction time of 15 h (Ni−P-T-15 h) shows the largest capacitive diameter among these four multilayer coatings.

For the EIS spectra shown in Figure 10, the equivalent circuits shown in Figure 11 were applied to analyze the experimental data in which $R_s$ is the solution resistance, CPE_{film} and $R_{film}$ are the capacitance and resistance of magnesium oxide or hydroxide, hydrothermal oxide layer, and Ni−P layer on the magnesium substrate, CPE_{super} and $R_{super}$ are the capacitance and resistance of the superhydrophobic layer, and CPE_{E} and $R_{E}$ are the double electric layer capacitance and charge transfer resistance of the AZ61 substrate. The fitting parameters of the AZ61 substrate, Ni−P coating, and Ni−P-T coatings in 3.5% NaCl solution are shown in Table 2. The inhibition efficiency of multilayer coating to AZ61 substrate was calculated using the following equation:33

$$
\eta_2 = \left( \frac{R_{total}^{coating} - R_{total}^{substrate}}{R_{total}^{coating}} \right) \times 100%
$$

where ($R_{total}^{substrate}$) and ($R_{total}^{coating}$) are the total corrosion resistance of the AZ61 substrate ($R_{total}^{substrate} = R_{film}^{substrate} + R_{ct}$) and Ni−P coating ($R_{total}^{coating} = R_{film}^{coating} + R_{ct}$) respectively, in 3.5% NaCl solution. From Table 2, it can be seen that the inhibition efficiency of multilayer coating to the AZ61 substrate varies in the range of 98.43−99.99%, which indicates that the Ni−P−T coating after hydrothermal treatment has a better protection effect on the AZ61 alloy. The Ni−P−T coating with a hydrothermal time of 15 h has the largest inhibition efficiency among these four coatings, which is consistent with the inhibition efficiency obtained from the polarization curve summarized in Table 1.

Figure 12 shows the data of $R_{super}$, $R_{film}$, and $R_{ct}$ for Ni−P−T coatings, and they increased at first and then decreased with
Overall, the corrosion resistance of Ni(1.6 × 10^3 Ω·cm²) is illustrated in Figure 13. First, a Ni–P coating with nodular structures and micro pores is grown on the AZ61 substrate because of the dissolution of the magnesium substrate and the evolution of hydrogen in the plating bath during electroless plating.25,34 and thus the as-prepared Ni–P coating has a limited protection effect on magnesium alloy (Figures 9 and 10, Tables 1 and 2). Second, a hydrothermal post-treatment is carried out on the surface of magnesium alloy with Ni–P coatings. During the hydrothermal reaction, H₂O is reacted with Ni²⁺ ions from the Ni(NO₃)₂ component to form Ni₃(NO₃)₂(OH)₄. The Ni₃(NO₃)₂(OH)₄ particles prefer to deposit in the site of micropores owing to the relatively low energy barrier in the areas, so the micro pores in the Ni–P coating are gradually covered by the Ni₃(NO₃)₂(OH)₄ particles. Thus the Ni₃(NO₃)₂(OH)₄ particles start to deposit on the whole coating surface after the micro pores are fully covered. With the increasing deposition time, the Ni(NO₃)₂ content in the solution decreases, and a Ni₃(NO₃)₂(OH)₄ nanosheet is grown on the top of the dense Ni₃(NO₃)₂(OH)₄ film due to the lower nucleation rate and crystal growth rate of Ni₃(NO₃)₂(OH)₄.35 Thus, the multilayer coating is composed of an inner dense Ni₃(NO₃)₂(OH)₄ layer and a porous outer Ni₃(NO₃)₂(OH)₄ nanosheet (Figure 3). In the meantime, the dissolved stearic acid molecules in the hydrothermal solution react with Ni²⁺ to form Ni(CH₃(CH₂)₁₆COO)₂ during the hydrothermal process, and thus a superhydrophobic layer is formed on the top of the multilayer coating (Figures 5 and 6).

3. DISCUSSION

The above experimental results show that the prepared Ni–P coating has a limited protection effect on the magnesium alloy because of the micropores on the electroless Ni–P coating. After hydrothermal treatment, micro pores are repaired by the Ni₃(NO₃)₂(OH)₄ layer with superhydrophobic characters, and the corrosion resistance of the magnesium alloy is greatly improved.

The evolving route of multilayer coating on magnesium alloy is illustrated in Figure 13. First, a Ni–P coating with nodular structures and micro pores is grown on the AZ61 substrate because of the dissolution of the magnesium substrate and the evolution of hydrogen in the plating bath during electroless plating,25,34 and thus the as-prepared Ni–P coating has a limited protection effect on magnesium alloy (Figures 9 and 10, Tables 1 and 2). Second, a hydrothermal post-treatment is carried out on the surface of magnesium alloy with Ni–P coatings. During the hydrothermal reaction, H₂O is reacted with Ni²⁺ ions from the Ni(NO₃)₂ component to form Ni₃(NO₃)₂(OH)₄. The Ni₃(NO₃)₂(OH)₄ particles prefer to deposit in the site of micropores owing to the relatively low energy barrier in the areas, so the micro pores in the Ni–P coating are gradually covered by the Ni₃(NO₃)₂(OH)₄ particles. Thus the Ni₃(NO₃)₂(OH)₄ particles start to deposit on the whole coating surface after the micro pores are fully covered. With the increasing deposition time, the Ni(NO₃)₂ content in the solution decreases, and a Ni₃(NO₃)₂(OH)₄ nanosheet is grown on the top of the dense Ni₃(NO₃)₂(OH)₄ film due to the lower nucleation rate and crystal growth rate of Ni₃(NO₃)₂(OH)₄.35 Thus, the multilayer coating is composed of an inner dense Ni₃(NO₃)₂(OH)₄ layer and a porous outer Ni₃(NO₃)₂(OH)₄ nanosheet (Figure 3). In the meantime, the dissolved stearic acid molecules in the hydrothermal solution react with Ni²⁺ to form Ni(CH₃(CH₂)₁₆COO)₂ during the hydrothermal process, and thus a superhydrophobic layer is formed on the top of the multilayer coating (Figures 5 and 6).

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Table 2. EIS Fitting Parameters of the AZ61 Substrate, Ni–P Coating, and Ni–P–T Coatings in 3.5% NaCl Solution

| Coating          | Rs (Ω·cm²) | Qsuper–Yp (A/cm²) | nsuper | Rsuper (Ω·cm²) | Qslim–Yp (A/cm²) | nslim | Rdlim (Ω·cm²) | Qsl (A/cm²) | nsl | Rsl (Ω·cm²) | η (%) |
|------------------|------------|-------------------|--------|---------------|-----------------|-------|--------------|-------------|-----|------------|-------|
| AZ61 substrate   | 13.3       |                   |        |               |                 |       |              |             |     |            |       |
| Ni–P             | 10.2       |                   |        |               |                 |       |              |             |     |            |       |
| Ni–P–T 9 h       | 1.0        | 3.9 × 10⁻⁸        | 0.9    | 1.6 × 10⁻⁴    | 1.5 × 10⁻³      | 0.9   | 5.6 × 10²    |             |     |            | 77.26 |
| Ni–P–T 12 h      | 1.0        | 1.5 × 10⁻⁹        | 0.9    | 9.1 × 10⁻⁴    | 6.9 × 10⁻⁸      | 0.6   | 4.0 × 10⁴    | 3.4 × 10⁻⁵ | 0.4 | 9.7 × 10⁴  | 98.43 |
| Ni–P–T 15 h      | 1.0        | 3.1 × 10⁻⁹        | 1.0    | 3.8 × 10⁻⁴    | 1.9 × 10⁻³      | 0.7   | 6.8 × 10⁵    | 1.5 × 10⁻⁶ | 0.6 | 5.1 × 10⁶  | 99.96 |
| Ni–P–T 18 h      | 1.0        | 2.4 × 10⁻⁷        | 0.8    | 3.6 × 10⁻⁴    | 1.9 × 10⁻⁷      | 0.8   | 7.2 × 10⁶    | 3.7 × 10⁻⁷ | 0.7 | 1.3 × 10⁷  | 99.98 |

Figure 11. Equivalent circuits for EIS spectra of Ni–P coating before and after post-treatment with 3.5 wt % NaCl solution: (a) AZ61 substrate, (b) Ni–P coating, and (c) Ni–P–T coatings.

Figure 12. Variations of Rs, Rdlim, and Rsl for Ni–P–T coatings.
Under different reaction times in the hydrothermal solution, different surface morphologies, wettabilities, and corrosion performances are obtained. With the increasing reaction time, the thickness and size of deposited Ni(\(\text{CH}_3\text{(CH}_2\text{)}_{16}\text{COO})_2\)) increase (Figures 2 and 3), but the contact angle increases at first and then decreases. Among these four reaction times, the multilayer coating at a reaction time of 15 h has the largest corrosion resistance (Figures 9, 10, and 12).

To investigate the structure and composition changes of the superhydrophobic surface after immersion, Raman and XPS analyses were conducted as shown in Figures S1 and S2. The results show that the Ni\(_3(\text{NO}_3)_2(\text{OH})_4\) nanosheets gradually dissolve after soaking in NaCl solution, causing the water contact angle to get reduced, and Cl\(^-\) ions gradually infiltrate from the layer surface to the substrate, causing corrosion to occur.

### 4. CONCLUSIONS

A superhydrophobic multilayer coating with high corrosion resistance was successfully prepared on the AZ61 magnesium alloy by electroless plating and a hydrothermal method. The prepared multilayer coating is composed of the electroless Ni–P coating, the dense Ni\(_3(\text{NO}_3)_2(\text{OH})_4\) layer, the porous Ni\(_3(\text{NO}_3)_2(\text{OH})_4\) nanostructure, and the stearic absorbing layers. The static contact angle and corrosion resistance of the multilayer coating increase first and then decrease with the increase in the hydrothermal reaction time. The optimum hydrothermal reaction time is 15 h, and the multilayer coating prepared under this condition has the highest corrosion resistance and the highest contact angle. During the hydrothermal post-treatment process, the micropores and defects on the Ni–P coating are repaired, and a dense Ni\(_3(\text{NO}_3)_2(\text{OH})_4\) layer and a superhydrophobic layer are formed on the top of the Ni–P coating, so the corrosion resistance of the substrate greatly improves.

### 5. EXPERIMENTAL SECTION

#### 5.1. Materials

The chemical composition of the AZ61 magnesium alloy was 5.92 wt % Al, 0.49 wt % Zn, 0.15 wt % Mn, 0.037 wt % Si, 0.003 wt % Cu, 0.007 wt % Fe, and balance Mg. The dimensions of all samples were 10 mm × 10 mm × 4 mm. All of the reagents were analytical grade, and deionized water with a resistivity of 18.2 M\(\Omega\)·cm was used in all experiments. The substrates were mechanically ground with SiC papers of successively finer grit down to 2000 grit, ultrasonically degreased for 10 min in acetone, and dried in air.

#### 5.2. Electroless Ni–P Coating

The pretreatment of the AZ61 magnesium alloy is essential before electroless plating. The process of pretreatment is as follows: alkaline cleaning → pickling → activation, with water washing after each step. The detailed operational conditions are listed in Table 3. Then, the substrate was put into an electroless nickel bath immediately after pretreatment. The electroless plating bath used consisted of 20 g/L NiSO\(_4\)·6H\(_2\)O, 20 g/L Na\(_2\)PO\(_4\)·12H\(_2\)O, 5 g/L H\(_3\)C\(_6\)H\(_5\)O\(_7\), 10 g/L NH\(_4\)HF\(_2\), 12 mL/L HF, and 15 g/L CH\(_3\)COONH\(_4\) under a pH value of 6.0, which was adjusted by the addition of NH\(_3\)·H\(_2\)O. The temperature of the plating bath was 85 °C, and the plating time was 120 min. After plating, the sample was taken from the bath and then cleaned with deionized water and dried with an electric dryer.

#### 5.3. Post-Treatment

After electroless plating, a hydrothermal treatment was carried out on the magnesium alloy with Ni–P coating. First, 0.025 M Ni(NO\(_3\))\(_2\)·6H\(_2\)O and an amount of stearic acid was dissolved into 50 mL of pure ethanol under vigorous stirring. After stirring for 20 min, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 100 mL, and a piece of electroless Ni–P coating was immersed into it. The autoclave was tightly sealed and heated at 120 °C for 9 ~ 18 h in an oven and then cooled down to room temperature naturally. The sample was taken out and rinsed with deionized water several times and then dried using an electric dryer.

#### 5.4. Characterization

The surface morphology was observed using a Hitachi S-4800 field-emission scanning electron microscopy (FESEM) operated at 5.0 kV. The structure of the coating was characterized using a D/MAX-2500 X-ray diffractometer. The functional groups on the coating were identified using infrared spectroscope and a DXR micro-Raman spectrometer (with an excitation wavelength of 532 nm). The state of the elements present in the outermost parts of the coating was identified using a Bio-Rad 3000 Fourier-transform infrared spectroscopy.
investigated by XPS measurements using an ESCALAB 250Xi. High-resolution spectra of the C1s signals were recorded in 0.100 eV steps with a pass energy of 20 eV.

The water contact angle and the sliding angle were measured with a waterdrop volume of 7 µL using a JC2000D optical contact angle meter at an ambient temperature. In addition, the contact angles of the superhydrophobic film in solutions with different pH values ranging from 1 to 14 were measured. The pH value of the solution was adjusted using hydrochloric acid and sodium hydroxide. The values reported are average of five measurements made on different positions of the sample surface.

The polarization curve and EIS spectra of the AZ61 substrate and Ni–P coating before and after post-treatment were measured in 3.5% NaCl solution at room temperature using an Autolab 302 electrochemical workstation. A three-electrode system with the sample having an exposed area of 1 cm² as the working electrode, a platinum electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode was employed in the test. The corrosion potential (Ecorr) and corrosion current density (icorr) were determined using the Tafel extrapolation method.

The potentiodynamic polarization experiments were performed at a scan rate of 0.1667 mV/s. EIS measurements were carried out at the open-circuit potential with a 10 mV amplitude AC signal, and the applied frequency ranged from 100 kHz to 0.01 Hz. The electrochemical parameters for the EIS data were calculated using ZSimpWin software using the given equivalent circuits.

■ ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02196.

Raman spectra of the superhydrophobic film before and after immersion, XPS full surface spectra of the superhydrophobic film before and after immersion, and the content of C, O, N, Ni, and Mg on the superhydrophobic film surface before and after immersion (PDF)

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Notes

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