

Effect of Magnesium Phosphate Anodizing Electrolyte on Corrosion Resistance of Aluminum Alloy

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Anodizing is one of the methods to improve the corrosion resistance of aluminum alloy. Anodic oxide film was prepared on 2024 aluminum alloy by constant current anodic oxidation method. The selected electrolyte was tartrate-sulfuric-acid electrolyte which adding magnesium phosphate. Anodic oxide film was prepared by changing the anodic oxidation temperature, current, time and other process parameters. The morphology, elemental composition and phase of anodic oxide film before and after optimization were characterized by SEM (scanning electron microscopy), XRD (X-ray diffraction) and EDS (energy dispersive spectroscopy), the corrosion resistance of anodic oxide film was characterized by electrochemical test, salt spray experiment and immersion aging experiment. The results showed that the thickness of the film after adding magnesium phosphate was higher than that before adding magnesium phosphate. Electrochemical impedance spectroscopy showed that the impedance modulus at 0.01 Hz is one order of magnitude higher after adding magnesium phosphate than before adding magnesium, and two orders of magnitude higher than the bare substrate, indicating that the corrosion resistance was greatly enhanced. The anodic oxide film obtained by adding magnesium phosphate to the electrolyte greatly improved the corrosion resistance, which provide an effective idea for the corrosion protection of aluminum alloy.

Keywords: aluminum alloy, anodizing, magnesium phosphate, anodic oxide film, improve corrosion resistance

Introduction

The 2024 aluminum alloy is a kind of alloy with high strength, good plasticity, excellent processability and good tensile properties, which plays an important role in military industry, manufacturing industry and other fields.¹ However, the poor corrosion resistance of 2024 aluminum alloy has a great impact on its service effect, which limits its wider application prospects.² Sacrificial anode, preparing coating and other methods were used to extend their service life, but did not achieved ideal effect.³ The surface treatment method of aluminum alloy are constantly innovative with the progress of science and technology, and anodizing

method is considered to be one of the methods which can effectively improve the corrosion resistance of aluminum alloy.⁴

The process of anodizing aluminum alloy included the formation, dissolution and stability of film. In the early stage, the oxide film grew continuously and the thickness of film increased gradually.⁵ The ion migration begins to be blocked when the film increases to a certain thickness. The dissolution rate of electrolyte gradually increases, finally reaches equilibrium with the growth rate, and the oxide film tends to be stable.⁶ Therefore the growth of film can be promoted by increasing the conductivity and decreasing the dissolution rate of the electrolyte.⁷ The traditional anodic oxidation electrolyte is a single type of acidic electrolyte, such as sulfuric acid, oxalic acid electrolyte, which is affected by temperature, concentration

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and other factors.⁸ Some scholars⁹ have found that adding an appropriate amount of organic acid to a single type of acidic electrolyte can weak the solubility of inorganic acids, reduce the porosity of the oxide film, and improve some performance of the film. Ma and co-workers¹⁰ have found that adding tartaric acid can generate dense anodic oxide film with small porosity on the surface of 2XXX aluminum alloy, improve the corrosion resistance and hardness of the film by comparing sulfuric acid and tartaric acid-sulfuric acid electrolytes. Zhou *et al.*¹¹ also have found that adding oxalic and tartaric acids mixture to sulfuric acid as base of anodic oxidation electrolyte, it can significantly increase the thickness and hardness of anodic oxide film for 2024 aluminum alloy, thus showing better corrosion resistance.

In recent years, adding inorganic additives to anodic oxidation electrolyte has been proved to improve the performance of anodic oxide film for aluminum alloy. At present, the most inorganic additives, such as heavy and rare earth metal salts, are usually used, which will promote the film performance mainly through physical and chemical adsorptions on the surface of anodic oxide film to reduce porosity. Li *et al.*¹² have found that adding cerium salt to sulfuric acid electrolyte can improve the internal stress of the oxide film, cerium ion of electrolyte can improve the current efficiency, reduce the surface porosity of the film, and increase the thickness of the barrier film. However, rare earth and heavy metal salts are expensive and environmentally unfriendly.

Phosphate and magnesium salts are regarded as additives that have the potential to substitute the limitation of heavy and rare earth metal salts. The mechanism which phosphate ions enhance the corrosion resistance of anodic oxide film is mainly reflected in the passivation effect and electrochemical behavior.¹³ For instance, Vippola *et al.*¹⁴ pointed out that phosphate ions would participate in the formation process of anodic oxide film, and would combine with Al^{3+} to form AlPO_4 or phosphorus-containing complex oxides. Their chemical stability phosphate ions are stronger than that of the main component of film, resulting in forming passivation film on the surface. The passivation film would inhibit the dissolution of anodic oxide film for aluminum alloy and the inward diffusion of corrosive media.¹⁵ Magnesium salt mainly reduce the pore of anodic oxide film through chemical precipitation reactions or physical adsorption and permeation, resulting in its corrosion resistance enhancement.¹⁶ According to the advantage of phosphate and magnesium salts, it may greatly improve the corrosion resistance of anodic oxide film if phosphate and magnesium are combined. Therefore, in this paper, an appropriate amount of magnesium phosphate was added to on the basis of anodizing 2024 aluminum

alloy with sulfuric acid-tartaric acid electrolyte, which take into account low cost and strong electrical conductivity of magnesium salt. The properties of anodic oxide film before and after adding magnesium phosphate were compared during the experiment. The surface and cross-section morphology, elemental composition and phase structure of anodic oxide film were characterized. The optimal current, temperature, and anodic oxidation time were investigated by electrochemical testing, and the corrosion resistance of the film was characterized by salt spray experiment and immersion aging experiment.

Experimental

Chemicals and materials

Sulfuric acid, tartaric acid, magnesium phosphate, sodium hydroxide, nitric acid, anhydrous ethanol, and sodium chloride, which were produced by Sinopharm Group Chemical Reagent Co., Ltd., were selected for experimental chemicals. The 2024 aluminum alloy which is produced by Northeast Aluminum industry, epoxy resin, conductive adhesive, silicone rubber, several copper wires, one platinum electrode were selected for experimental materials.

Experimental procedure

The 2024 aluminum alloy were cut into circle with a diameter of 14 mm by wire cutting equipment, and were adhered to the copper wire with conductive glue. Then the aluminum electrode were made by adding PVC (polyvinylchloride) pipe to epoxy packaging, and the surface was polished to mirror surface by grinding and polishing machine. The sample were washed in 10 wt.% NaOH solution for 90 s, then were pickled in 70 wt.% nitric acid for 30 s. The samples were ultrasonically washed in anhydrous ethanol for 10 min, dried and set aside for later experiment.

An amount of 79.5 g tartaric acid and 46 g concentrated sulfuric acid were fully dissolved in water, and then 20 g magnesium phosphate powder was added to the mixed acid solution. The volume of electrolyte was fixed to 1000 mL. After the powder was completely dissolved, the anodic oxidation electrolyte has been prepared, then the anodic oxidation process was carried out.

GW INSTEK PSW250-9 anodic oxidation power supply was used for anodic oxidation process. In constant current mode, aluminum alloy was used as anode, platinum electrode as cathode, and the mixed electrolyte as anode oxidation electrolyte. The anodic oxidation current was adjusted to 0.194, 0.207 and 0.221 A, the anodic oxidation

temperature was at the range of 27–42 °C, and the anodic oxidation time was 33–42 min. The anodized samples were washed under distilled water and dried with a hairdryer.

Characterization and experiment

Hitachi Regulus 8100 scanning electron microscope was used to observe the surface and cross-section morphology of samples, and point scan and surface scan of energy spectrum were used to study the elemental composition of surface film. Smart Lab X-ray diffractometer was used to further analyze the composition of surface film. YWX/Q-250 salt spray tank was used to conduct salt spray experiment for the samples. The salt spray environment was atomized by 3.5 wt.% NaCl solution, and the samples were soaked in 3.5 wt.% NaCl solution for aging experiment.

The electrochemical impedance test was carried out by the electrochemical workstation produced by Wuhan Corrtest Instruments Co., Ltd. to characterize the corrosion resistance of samples. The electrochemical impedance test was carried out at room temperature in a three-electrode system with saturated Ag/AgCl electrode as reference electrode, platinum electrode as auxiliary electrode, and 3.5 wt.% NaCl as electrolyte. The scanning frequency range was 10^{-2} – 10^5 Hz, the AC amplitude was 10 mV, and the scanning point was 70.

Results and Discussion

Influence of electrolyte composition on anodic oxide film of 2024 aluminum alloy

Firstly, a mixed solution of tartaric acid and sulfuric acid was used as the electrolyte, and the prepared samples were taken as the blank control group for comparison with the samples prepared after the subsequent addition of magnesium phosphate.

As shown in Figure 1a, the anodic oxide film generated by the anodic oxidation electrolyte with tartaric acid added under a constant pressure mode has a relatively single film structure and a relatively dense pore distribution. The surface of the bare aluminum alloy substrate in Figure 1b is relatively smooth. The Nyquist plot results of the electrochemical impedance spectrum are shown in Figure 1c, where the corrosion resistance is represented by the radius of the arc. It can be seen that, the corrosion resistance of the anodic oxide film is much greater than that of the bare substrate after adding tartaric acid, and it also exceeds the corrosion resistance of anodic oxide film prepared solely with sulfuric acid electrolyte in the literature.¹⁷

The electrolyte of tartaric acid-sulfuric acid mixed system enhances the corrosion resistance of 2024 aluminum

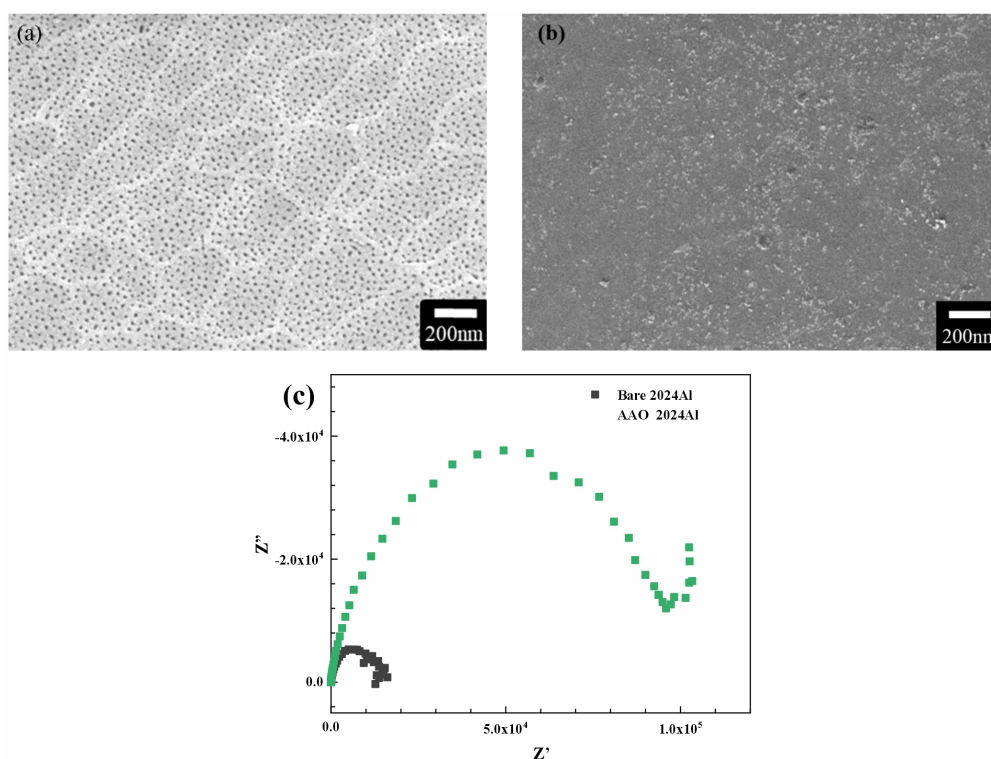


Figure 1. (a) SEM morphology of anodic oxide film surface in the constant pressure mode of tartaric acid-sulfuric acid electrolyte; (b) SEM morphology of bare aluminum alloy; (c) comparison of electrochemical impedance spectra between the 2024 aluminum alloy bare substrate and anodic oxide film in the sulfuric acid-tartaric acid system.

alloy. However, compared with the impedance value exceeding $105 \Omega \text{ cm}^{-2}$ of the traditional spray painting method, the extent to which the corrosion resistance is improved is limited. To further improve the corrosion resistance, magnesium phosphate metal salt was added to the electrolyte, and anodic oxidation was first carried out in a constant voltage mode. It was found that the anodic oxide film could not be effectively formed at a voltage of 14 V. Considering that the addition of magnesium phosphate might have a certain impact on the conductivity, the anodic oxidation voltage and the addition amount of magnesium phosphate were increased. It was found that the formation process of the film was unstable when the concentration of magnesium phosphate increased to 20 g L^{-1} and the anodic oxidation voltage rose to 29 and 30 V. There were a large number of corrosion pits on the surface of generated samples, and there were severely corroded and damaged as shown in Figure 2.

Three sets of parallel experiments were conducted on the samples of 29 and 30 V, and they were marked as 1, 2 and 3, respectively. It can be seen from the time-current curve in Figures 3a and 3b that the samples can form anodic

oxide film under the same voltage condition. The time-current curve shows a relatively gentle and stable trend, indicating that the anodic oxide film is growing steadily. However, the current will suddenly increase to more than 1 A over time when the same voltage conditions are applied. At this point, the surface of the generated sample presents an ablated morphology, resulting in the failure of preparing anodic oxide film.

The anodic oxidation mode was changed to constant current mode because the samples could not be stably prepared under the constant pressure mode. The temperature and time of experiment remained constant. It was found that the anodic oxidation process was milder and the results were more stable under the mode of constant current. At a current of 0.12 A cm^{-2} , while keeping other conditions the same, 5, 10, 15 and 20 g of magnesium phosphate were added to 1000 mL of tartaric acid-sulfuric acid mixed solution. It was observed that with the increase of the concentration of added magnesium phosphate, there was a tendency for a gradual film formation on the sample surface. When the concentration was 20 g L^{-1} , it was observed that the surface of the

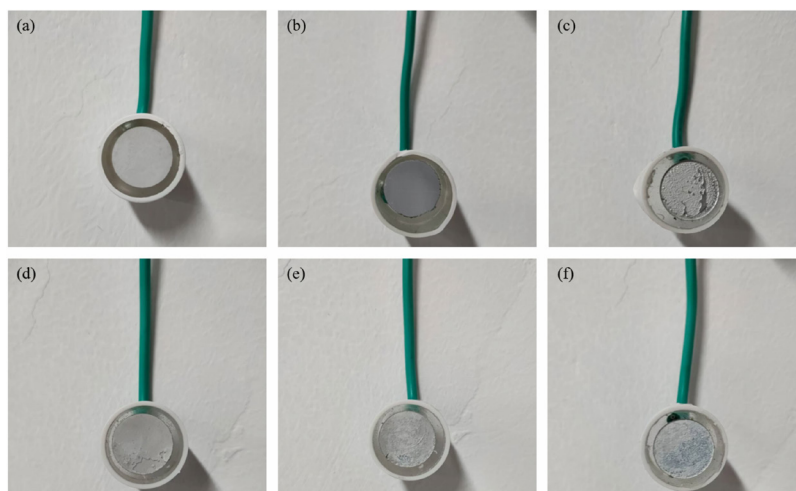


Figure 2. Macroscopic morphology of the sample surface at (a-c) 29 V and (d-f) 30 V at the same temperature.

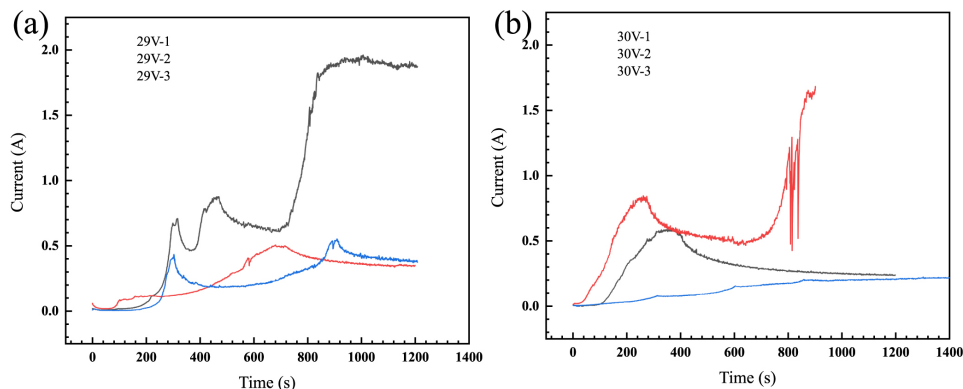


Figure 3. Time-current curve at (a) 29 V and (b) 30 V.

samples were completely covered, and no bare aluminum alloy substrate appeared. The surface of the samples prepared with a magnesium phosphate concentration of 20 g L^{-1} was observed by scanning electron microscopy, and the results were shown in Figure 4.

The SEM (scanning electron microscopy) results show that after adding magnesium phosphate, the surface of the aluminum alloy is covered with film. The majority of film is a relatively flat structure. No characteristic pore structure of the anodized film can be observed at the flat area, while the film has a few defects, such as the c area marked in Figure 4a. The magnified morphology of the defect area is shown in Figure 4c. It can be seen that the shape is similar to a honeycomb structure, porous and the pores are regularly circular, indicating that the defect area is an exposed anodic oxide film, while the flat area has the pores covered, thus achieving the sealing of the pores.

In order to characterize the elemental composition of the film prepared in the sulfuric acid-tartaric acid-magnesium phosphate system, point scanning and surface scanning of the film were conducted. The result of the surface scan is shown in Figures 5a and 5b. It can be seen that the elements contained in the film are mainly Al and O elements, indicating that the main composition of the film is Al_2O_3 . The results of the point scan are shown in Figure 5c. It can be seen that in addition to Al and O elements, the surface of the film also contains Mg and P. It is speculated that after the addition of magnesium

phosphate, magnesium phosphate participates in the reaction of the anodic oxide film and constitutes some structural substances in the sealing film.

Figure 6 shows the cross-sectional thickness of film. Generally speaking, the thickness of the anodic oxide film formed in the tartaric acid-sulfuric acid system is approximately $30 \mu\text{m}$. However, after adding magnesium phosphate, the thickness of the anodic oxide film and the sealing film reaches $111.66 \mu\text{m}$, which is much higher than that of the anodic oxide film without adding magnesium phosphate. The thicker anodic oxide film with obviously blocking effect on external corrosive media, the stronger corrosion protection performance of aluminum alloys would be.¹⁸

It can be seen from the XRD (X-ray diffraction pattern) results in Figure 7a that the main diffraction peaks of the surface anodic oxide film are around 39° , 45° , 65° and 78° . According to the reference materials, these respectively correspond to the characteristic peaks of the (111), (200), (220) and (311) crystal planes of aluminum.¹⁹ The characteristic peaks of aluminum oxide do not appear in the XRD results. In order to eliminate the interference of the aluminum alloy surface on the XRD results, the anodic oxide film on the surface of the aluminum alloy after anodic oxidation with magnesium phosphate was scraped into powder. XRD tests were conducted again using the powder as the raw material and compared with the anodic oxide film prepared by the tartaric acid-sulfuric acid system.

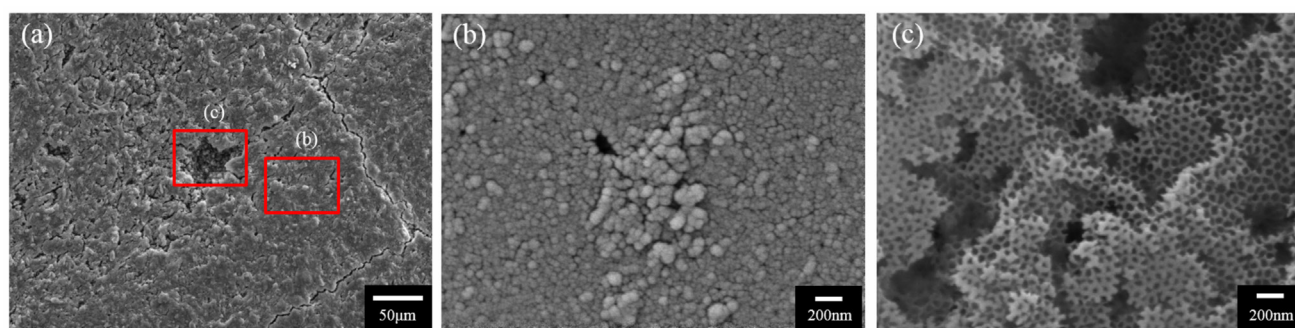


Figure 4. SEM surface morphology of the sample prepared by anodic oxidation after adding 20 g L^{-1} magnesium phosphate to the electrolyte: (a) overall morphology; (b) topography of the flat area; (c) morphology of the defect area.

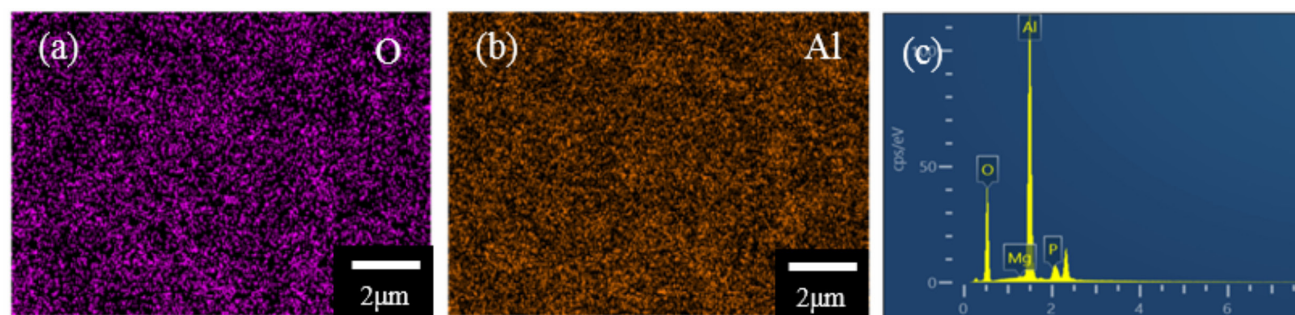


Figure 5. (a,b) EDS surface scanning result diagram; (c) EDS point scanning result.

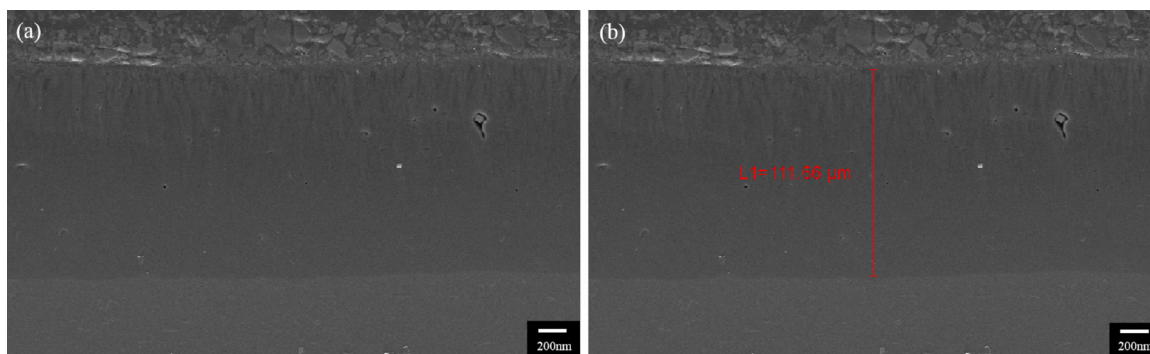


Figure 6. Cross-sectional (a) SEM and (b) thickness diagram of the anodic oxide film after adding magnesium phosphate.

The results are shown in Figure 7b. It can be observed that when magnesium phosphate is not added, two additional characteristic peaks are shown on XRD near 46° and 67° . After consulting the literature,²⁰ it is known that these are the Al_2O_3 peaks in the anodic oxide film, and the alumina mainly exists in the form of $\gamma\text{-Al}_2\text{O}_3$. However, after adding magnesium phosphate, no effective sharp diffraction peaks are detected in the anodic oxide film. It is speculated that the generated Al_2O_3 has poor crystallinity and exists in an amorphous form. Considering the addition of magnesium phosphate, both phosphate ions and magnesium ions have a promoting effect on the amorphous transformation of alumina. Phosphate ions tend to complex with aluminum ions during anodic oxidation, hindering the ordered arrangement of aluminum ions and thereby inhibiting the lattice growth of alumina. Additionally, the competitive process between phosphate and sulfate may interfere with the uniform deposition of alumina, exacerbating its amorphous state. Magnesium ions, on the other hand, are more likely to be considered for doping effects. During the anodic oxidation process, magnesium ions may embed into the structure of alumina, replacing some of the Al^{3+} sites, causing lattice distortion and inducing formation of amorphous alumina.

To further explore the chemical composition of the film formed after the addition of magnesium phosphate,

Fourier transform infrared spectroscopy tests were conducted on the thin sheets using a Fourier transform infrared spectrometer. The results are shown in Figure 7c. It can be seen from the infrared spectrum test graph of the film that the sample has a wide peak within the range of $400\text{--}800\text{ cm}^{-1}$, formed by the stretching vibration of the Al–O bond in amorphous alumina, and contains two sharp peaks of 621.1 and 777.8 cm^{-1} inside. Among them, the peak at 621.1 cm^{-1} may be related to the bending vibration of magnesium phosphate, magnesium hydroxide or aluminum phosphate salts. The peak at 777.8 cm^{-1} may correspond to the stretching vibration of Al–O–P. There is one characteristic peak at 1112.6 cm^{-1} , corresponding to the asymmetric stretching vibration of phosphate ions. It indicates that phosphate ions are involved in the formation process of the film. The characteristic peak at 1350 cm^{-1} corresponds to the stretching vibration of the P=O bond in phosphate, while the characteristic peak at 1630 cm^{-1} corresponds to the bending vibration of H–O–H in water. There is a wide peak at $3000\text{--}3600\text{ cm}^{-1}$ due to the easy adsorption of water or hydroxy groups on the surface of amorphous alumina.²⁰ The results of infrared spectroscopy indicate that the composition of the film is mainly aluminium oxide, which may contain sealing substances such as aluminium phosphate, magnesium phosphate, and magnesium hydroxide.

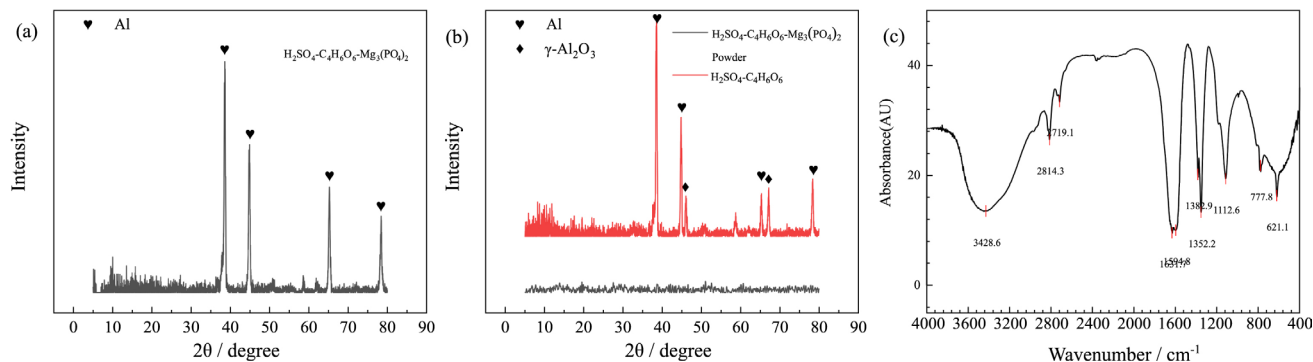


Figure 7. (a) XRD pattern of the anodized aluminum alloy sheet after adding magnesium phosphate; (b) XRD patterns of anodic oxide film powder before and after the addition of magnesium phosphate; (c) infrared spectrogram.

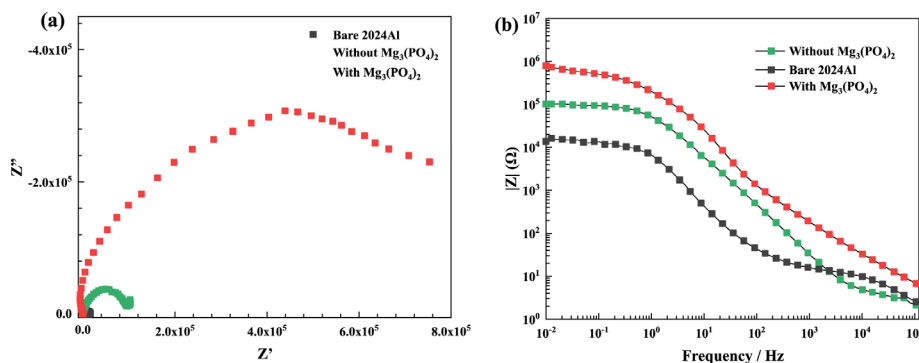


Figure 8. Comparison of electrochemical impedance spectra of bare substrate and anodized aluminum alloy before and after adding magnesium phosphate: (a) Nyquist chart; (b) Bode diagram.

The results of electrochemical impedance spectrum are shown in Figure 8. It can be seen that compared with Figure 8b, the arc radius of film after adding magnesium phosphate is much larger than that of anodic oxide film without adding magnesium phosphate, indicating that corrosion resistance of film prepared after adding magnesium phosphate has been greatly improved.²¹

In the Bode diagram, the impedance modulus at 0.01 Hz is generally taken as one of the reference standards for evaluating the corrosion resistance of the sample. As shown in Figure 8b, the impedance modulus of the sample after adding magnesium phosphate at 0.01 Hz exceeds $10^6 \Omega$, which is one order of magnitude higher than that without adding magnesium phosphate and two orders of magnitude higher than that of the aluminum alloy matrix. The above results indicate that the corrosion resistance of aluminum alloys are improved after adding magnesium phosphate.²²

Influence of current on corrosion resistance of 2024 aluminum alloy

By using the control variable method, the temperature of anodic oxidation electrolyte was controlled at 37 °C, the anodic oxidation time was 35 min, and the anodic oxidation current were changed to 0.126, 0.135, and 0.144 A cm⁻², that is, 0.194, 0.207, and 0.221 A, respectively. Electrochemical impedance spectroscopy analysis was conducted on the prepared samples.

The equivalent circuit diagram was shown in Figure 9. R_s (solution resistance), R_{ct} (charge transfer resistor), CPE (constant phase element) were included among equivalent circuit components.²³ The results of the electrochemical impedance spectroscopy show that in Figure 10a, as the current continuously increases, the EIS (electrochemical impedance spectroscopy) of all samples has only one capacitive reactance arc, and the arc radius is constantly increasing. The fitting data in Table 1 shows that as the anodic oxidation current continuously increases, the

charge transfer resistance of the samples also continuously increases. When the anodic oxidation current increases to 0.221 A, at this time, the charge transfer resistance R_{ct} is the largest among the three.

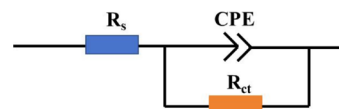


Figure 9. Fitting equivalent circuit diagram.

Table 1. Electrochemical fitting parameters of Nyquist diagrams of samples with different currents

Current / A	R_s / (Ω cm ²)	R_{ct} / (Ω cm ²)	CPE-T / (Ω^{-1} s ⁻ⁿ cm ⁻²)	n
0.194	250.2	2.61×10^5	3.35×10^{-6}	0.66
0.207	142.0	7.14×10^5	3.59×10^{-6}	0.63
0.221	576.4	1.40×10^6	2.38×10^{-6}	0.72

R_s : solution resistance; R_{ct} : charge transfer resistance; CPE-T: constant phase element; n: dimensionless parameter.

It can be seen that the impedance modulus at 0.01 Hz increases with the increase of the anodic oxidation current. Figure 10b further proves this point. The phase angle diagram is shown in Figure 10c. It can be seen that the peak width and peak height of the phase angle peak in the mid-frequency region also increase with the increase of the anodic oxidation current, which also proves that the corrosion resistance of the material increases with the increase of the oxidation current. The results show that when the anodic oxidation current reaches 0.221 A, the corrosion resistance of the sample is the strongest.

Influence of temperature on corrosion resistance of 2024 aluminum alloy

By using the control variable method, the anodic oxidation current was controlled at 0.221 A and the anodic oxidation time was 35 min. The electrolyte temperature was

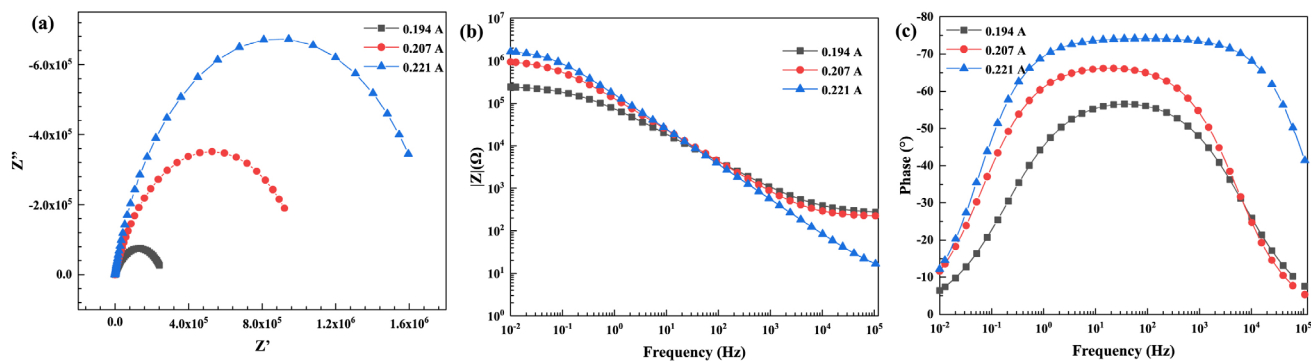


Figure 10. Comparison of electrochemical impedance spectra of samples with different currents: (a) Nyquist plot; (b) Bode diagram; (c) phase diagram.

changed to 27–42 °C through a constant temperature water bath with stirring, and the prepared samples were tested by electrochemical impedance spectroscopy.

In Figure 11a, the EIS of the samples at all temperature presents a constant time. Within the range of 27–37 °C, the arc radius of capacitive reactance increases with the rise of temperature. The results in Table 2 show that the charge transfer resistance of the sample increases with the rise in temperature at 27–37 °C, indicating that the corrosion resistance of the sample oxide film is improving within this temperature range. However, when the temperature continued to rise at 37 °C, it was found that the radius of the capacitive arc resistance decreased, which also indicated that the corrosion resistance of the sample decreased and accelerated the corrosion dissolution of the oxide film.

Both the Bode plot and the phase angle plot in Figures 11b and 11c show the same trend. When the temperature is 37 °C, it can be seen that the impedance modulus is the highest at 0.01 Hz at this time. Figure 12 and Table 3 show that at 37–42 °C, the charge transfer resistance of the sample decreases with the increase of temperature, indicating that the corrosion resistance of the sample within this temperature range decreases with the increase of temperature. The results of electrochemical impedance spectroscopy analysis show that when the temperature of the anode oxidation electrolyte of sulfuric acid-tartaric acid-magnesium phosphate is 37 °C, the

Table 2. Electrochemical fitting parameters of Nyquist diagrams of samples with different temperature

Temperature / °C	R_s / ($\Omega \text{ cm}^2$)	R_{ct} / ($\Omega \text{ cm}^2$)	CPE-T / ($\Omega^{-1} \text{ s}^{-n} \text{ cm}^{-2}$)	n
27	185.1	5.13×10^5	2.37×10^{-6}	0.78
29	116.1	1.49×10^6	1.89×10^{-6}	0.74
31	189.0	2.11×10^6	1.53×10^{-6}	0.71
33	112.0	2.50×10^6	2.47×10^{-6}	0.68
35	222.5	2.81×10^6	1.79×10^{-6}	0.72
37	147.9	3.44×10^6	1.67×10^{-6}	0.71

R_s : solution resistance; R_{ct} : charge transfer resistance; CPE-T: constant phase element; n: dimensionless parameter.

corrosion resistance of the prepared anodized aluminum alloy is the strongest.

Influence of anodic oxidation time on corrosion resistance of 2024 aluminum alloy

Considering that the addition of magnesium phosphate leads to a relatively thick sealing film above the anodic oxide film, the corrosion resistance of the samples should be the best when both the sealing film and the anodic oxide film reach a stable state. Therefore, the time-voltage curve of anodic oxidation of aluminum alloy after the addition of magnesium phosphate was tested, and the results are shown in Figure 13.

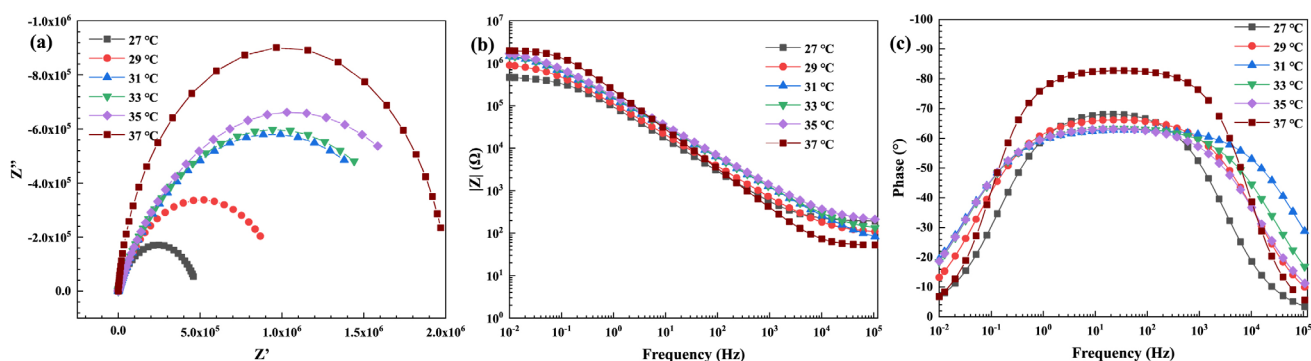


Figure 11. Comparison of electrochemical impedance spectra of samples with different temperatures: (a) Nyquist plot; (b) Bode diagram; (c) phase diagram.

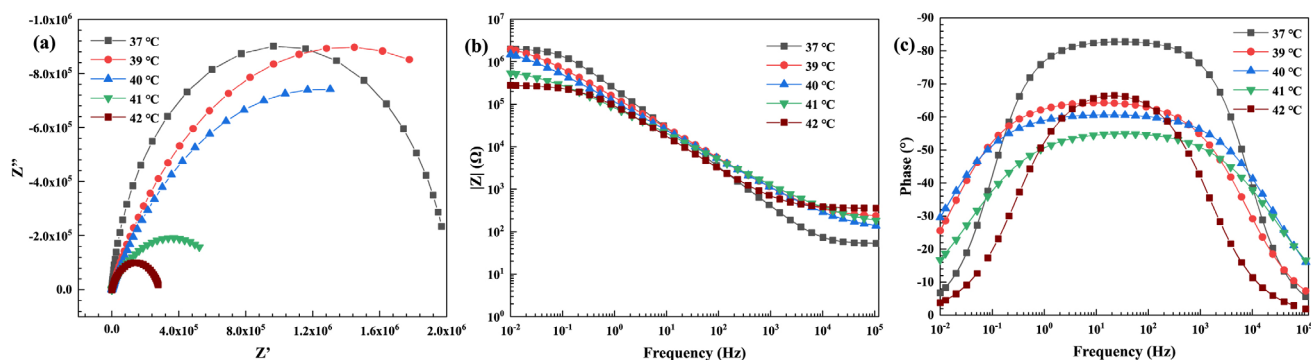


Figure 12. Comparison of electrochemical impedance spectra of samples with different temperatures: (a) Nyquist plot; (b) Bode diagram; (c) phase diagram.

Table 3. Electrochemical fitting parameters of Nyquist diagrams of samples with different temperature

Temperature / °C	$R_s / (\Omega \text{ cm}^2)$	$R_{ct} / (\Omega \text{ cm}^2)$	$\text{CPE-T} / (\Omega^{-1} \text{ s}^{-n} \text{ cm}^{-2})$	n
37	147.9	3.44×10^6	1.67×10^{-6}	0.71
39	125.3	3.31×10^6	1.71×10^{-6}	0.68
40	108.8	1.91×10^6	1.66×10^{-6}	0.71
41	142.0	7.14×10^5	3.59×10^{-6}	0.63
42	34.53	4.20×10^5	2.40×10^{-6}	0.72

R_s : solution resistance; R_{ct} : charge transfer resistance; CPE-T: constant phase element; n: dimensionless parameter.

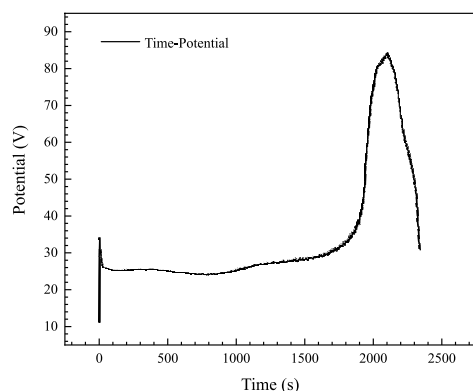


Figure 13. Time-voltage curve of the film preparation process.

From the time-voltage curve, it can be seen that after the addition of magnesium phosphate, it can roughly be divided into three stages: the first is the breakdown stage on the surface of the aluminum alloy, the second is the stable growth stage of the anodic oxide film, and the third is the dissolution stage of the anodic oxide film and the formation stage of the sealing film. During the third stage, as the thickness of the anodic oxide film gradually increases, the voltage required for the reaction will also rise slowly. The dissolution of the film begins to dominate. The dissolution of alumina causes a large amount of Al^{3+} to accumulate on the surface of the film, and a large amount of H^+ near the electrode is consumed, thereby leading to an increase in the local OH^- concentration. In addition,

the increase in voltage causes the local area temperature near the electrode to rise, providing favorable conditions for the sealing of phosphate ions and magnesium ions. The sealing film begins to form, and the formation of the sealing film means that the surface impedance of the sample increases, requiring a higher voltage for the reaction.²⁴ This is also the reason why the voltage rises to the peak in the later stage. Ultimately, as the reaction time continues to extend and the sealing film thickens, the reaction of alumina dissolving to form Al^{3+} will gradually weaken. This leads to an increase in the concentration of H^+ near the electrode, which will react with the sealing film and dissolve it, thereby causing the voltage to drop. Therefore, the anodic oxidation time should not be too long or too short. It can be roughly judged from the time-voltage curve that the anodic oxidation time with the thickest sealing film, that is, the strongest corrosion resistance, is approximately within the range of 33 to 42 min.

Therefore, by using the control variable method, the anodic oxidation current was controlled at 0.221 A, and the anodic oxidation time was changed to 33, 36, 39 and 42 min. To verify the accuracy of the results, the electrochemical impedance spectrum data at 30, 35 and 40 °C were all analyzed. The results of the electrochemical impedance spectroscopy are shown in Figure 14 and Table 4. During the anodic oxidation process in all temperature environments, the EIS of the sample shows a capacitive reactance arc. It can be seen from the radius of the capacitive reactance arc that when the anodic oxidation time is 36 min, the radius of the capacitive reactance arc is the largest, and the value of the charge transfer resistance fitted in the table is the largest at 36 min, indicating that the corrosion resistance of the sample is the best, and the conclusion is consistent in all temperature environments.

Figure 15, Tables 5 and 6 show Bode diagram and phase angle diagram. It can be seen that the impedance modulus of the samples prepared at 36 min is the largest at 0.01 Hz, indicating that the corrosion resistance of the sample is the

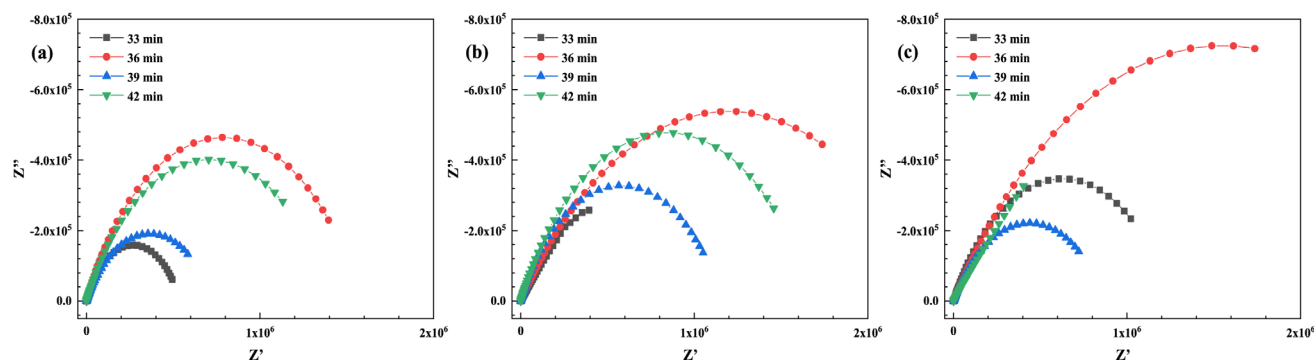


Figure 14. Comparison of electrochemical impedance spectra of samples with different treatment times at (a) 30 °C; (b) 35 °C; (c) 40 °C.

Table 4. Electrochemical fitting parameters of Nyquist diagrams of samples with different processing times (30 °C)

Time / min	$R_s / (\Omega \text{ cm}^2)$	$R_{ct} / (\Omega \text{ cm}^2)$	$\text{CPE-T} / (\Omega^{-1} \text{ s}^{-n} \text{ cm}^{-2})$	n
33	1.30	3.87×10^5	2.64×10^{-6}	0.74
36	82.39	2.21×10^6	1.99×10^{-6}	0.69
39	69.68	7.09×10^5	2.66×10^{-6}	0.70
42	47.23	1.36×10^6	1.76×10^{-6}	0.72

R_s : solution resistance; R_{ct} : charge transfer resistance; CPE-T: constant phase element; n: dimensionless parameter.

strongest. The phase angle diagram also shows that the medium-frequency peak height of the samples at 36 min is the highest, the optimal process time can be obtained as 36 min based on results of electrochemical impedance spectroscopy.

Results of salt spray experiment

In order to further explore the corrosion resistance of the anodized samples prepared by adding magnesium phosphate to the tartaric acid-sulfuric acid electrolyte, salt spray tests were adopted to simulate the usage environment of aluminum alloys. The standard adopted for the salt spray test is GB/T 10125-2021.²² The samples were treated with salt spray for 0, 2, 3, 5, 7 and 14 days. The macroscopic morphology of the samples is shown in Figure 16. The SEM test results are shown in Figure 17.

From the results of the macroscopic morphology map, it can be seen that with the extension of the salt spray test time, there is no significant difference in the macroscopic morphology of the sample at the beginning and after salt spray. The integrity of the film remains good, and there is

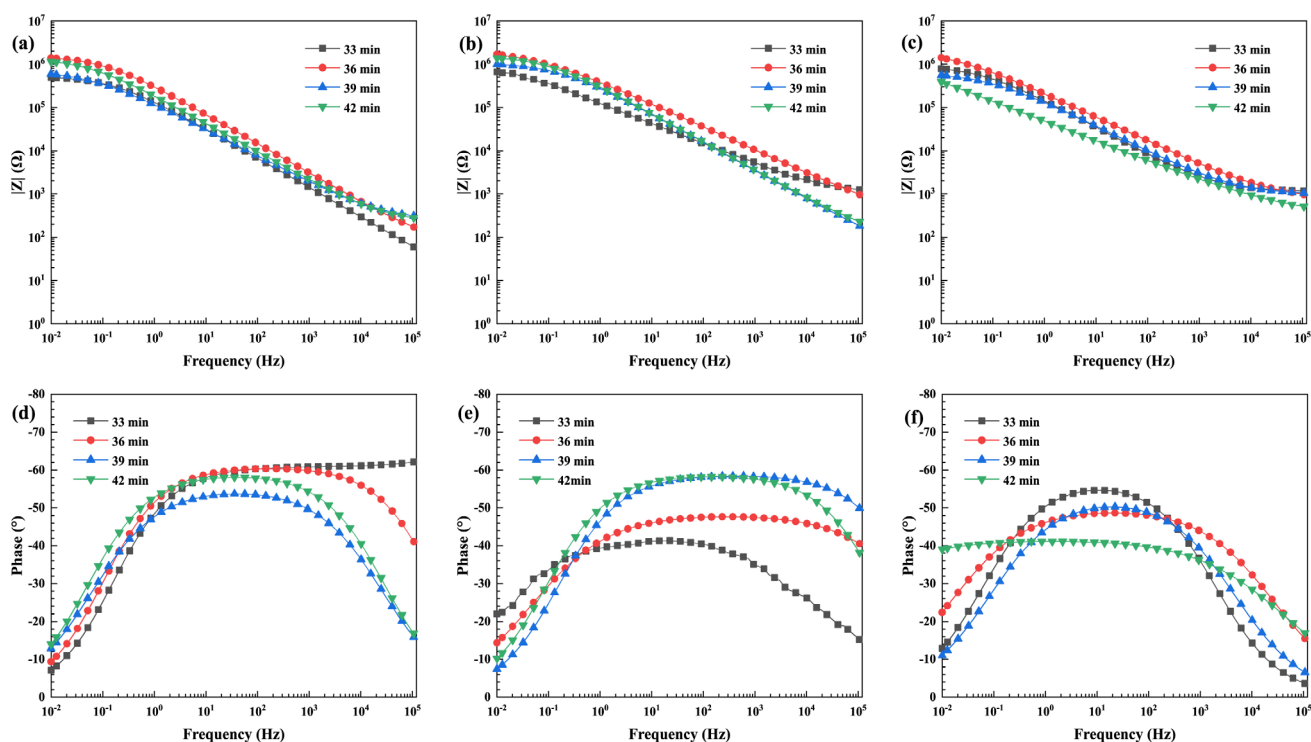


Figure 15. Comparison of electrochemical impedance spectra of samples with different treatment times at (a,d) 30 °C; (b,e) 35 °C; (c,f) 40 °C.

Table 5. Electrochemical fitting parameters of Nyquist diagrams of samples with different processing times (35 °C)

Time / min	$R_s / (\Omega \text{ cm}^2)$	$R_{ct} / (\Omega \text{ cm}^2)$	$\text{CPE-T} / (\Omega^{-1} \text{ s}^{-n} \text{ cm}^{-2})$	n
33	23.73	7.92×10^5	2.18×10^{-6}	0.73
36	27.73	2.05×10^6	2.01×10^{-6}	0.69
39	5.72	1.18×10^6	1.53×10^{-6}	0.82
42	7.58	1.74×10^6	1.26×10^{-6}	0.83

R_s : solution resistance; R_{ct} : charge transfer resistance; CPE-T: constant phase element; n: dimensionless parameter.

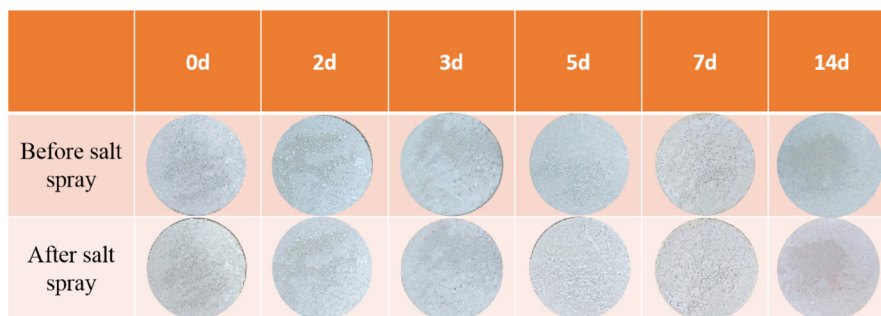
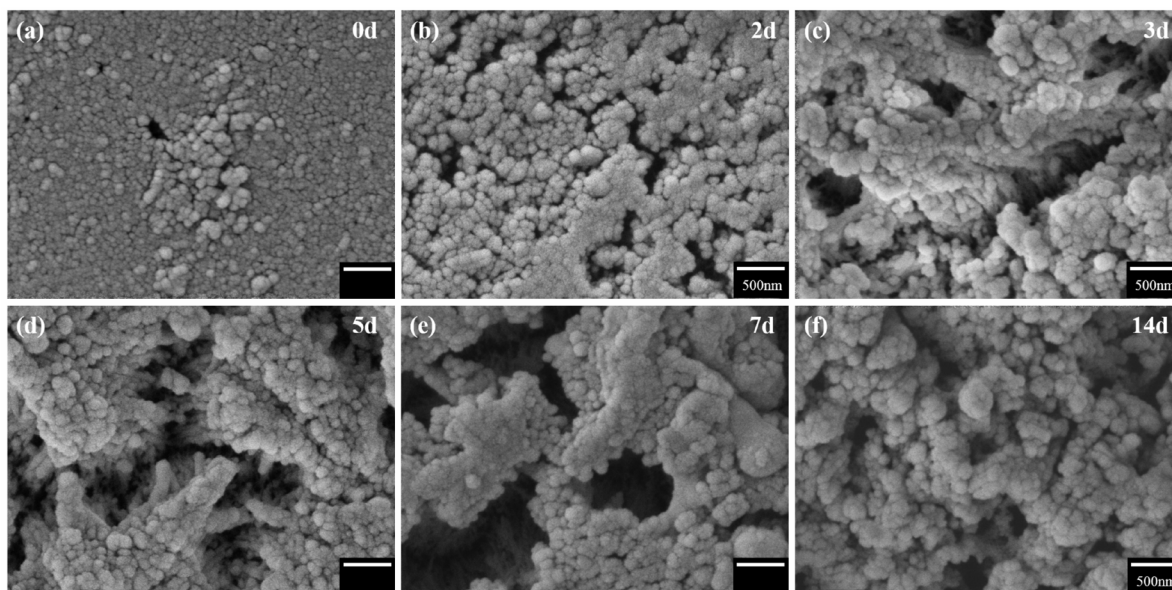
Table 6. Electrochemical fitting parameters of Nyquist diagrams of samples with different processing times (40 °C)

Time / min	$R_s / (\Omega \text{ cm}^2)$	$R_{ct} / (\Omega \text{ cm}^2)$	$\text{CPE-T} / (\Omega^{-1} \text{ s}^{-n} \text{ cm}^{-2})$	n
33	142.4	1.01×10^6	1.33×10^{-6}	0.78
36	58.36	4.05×10^6	2.01×10^{-6}	0.68
39	210.8	1.19×10^6	1.96×10^{-6}	0.71
42	151.1	1.87×10^6	1.64×10^{-6}	0.70

R_s : solution resistance; R_{ct} : charge transfer resistance; CPE-T: constant phase element; n: dimensionless parameter.

no phenomenon of corrosion peeling or exposure of the aluminum alloy substrate. It can be seen from the SEM results that with the continuous extension of salt spray time, although the corrosion phenomenon is constantly aggravating, the sealing film still exists. No characteristic honeycomb structure of the exposed aluminum alloy substrate and the anodized film was observed, indicating that the film still has corrosion resistance after 14 days of salt spray treatment.

The electrochemical test results are shown in Figure 18 and Table 7. With the extension of salt spray treatment time, the capacitive arc radius of the sample and the impedance modulus at 0.01 Hz are also decreasing, indicating that the corrosion resistance of the film is reducing. However, when the salt spray time was 14 days, the value was still higher than that of the anodic oxide film prepared by the tartaric acid-sulfuric acid system, indicating that the salt spray treatment would reduce the corrosion resistance of the anodic oxide film. But after 14 days, the anodic oxide film could still ensure the corrosion resistance strength of the aluminum alloy.

**Figure 16.** Macroscopic morphology and SEM results of salt spray test.**Figure 17.** SEM results of salt spray test of anodic oxide film: (a) 0; (b) 2; (c) 3; (d) 5; (e) 7; (f) 14 days.

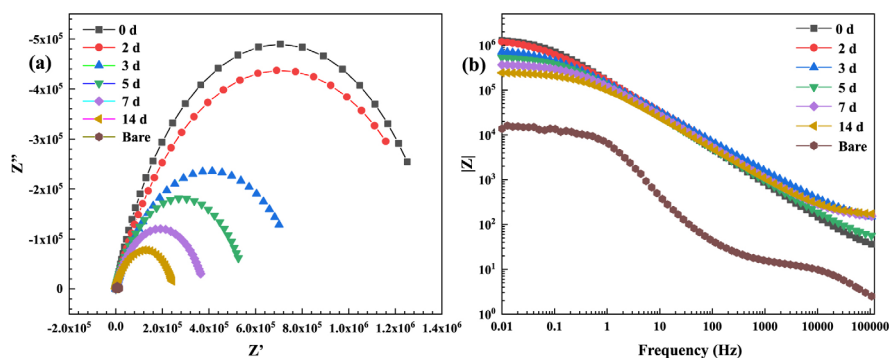


Figure 18. Comparison of electrochemical impedance spectra after salt spray treatment with different times: (a) Nyquist plot; (b) Bode diagram.

Table 7. Electrochemical fitting parameters of Nyquist diagrams of samples after different salt spray times

Time / days	$R_s / (\Omega \text{ cm}^2)$	$R_{ct} / (\Omega \text{ cm}^2)$	$\text{CPE-T} / (\Omega^{-1} \text{ s}^{-n} \text{ cm}^{-2})$	n
0	26.9	3.49×10^6	1.41×10^{-6}	0.71
2	67.6	2.54×10^6	1.49×10^{-6}	0.68
3	73.6	1.01×10^6	2.17×10^{-6}	0.69
5	130.9	7.47×10^5	2.19×10^{-6}	0.64
7	349	5.51×10^5	1.93×10^{-6}	0.69
14	358	2.57×10^5	3.81×10^{-6}	0.66
Bare Al	7.69	1.37×10^4	1.93×10^{-5}	0.85

R_s : solution resistance; R_{ct} : charge transfer resistance; CPE-T: constant phase element; n: dimensionless parameter.

Results of immersion aging experiment

The macroscopic morphology and SEM results of the samples after immersion aging experiment are shown in Figures 19 and 20.

The results of the macroscopic morphology show that the surface of anodic oxide film gradually become rough with the extension of the soaking time. On the 21st day of soaking, the surface roughness is most obvious, but there is no corrosion peeling or exposure of the aluminum alloy substrates. The results of SEM and weightlessness curves also confirm this point. The above results indicate that after 21 days of immersion aging experiment, the corrosion resistance of anodic oxide film has not been completely

destroyed, and the film can still resist the erosion of the corrosive environment.

Mechanism analysis for formation of anodic oxide film

Since phosphates and magnesium salts have been proven to have good sealing effects in previous studies, after adding magnesium phosphate, the anodic oxide film prepared under the synergistic action of phosphate ions and magnesium ions can be seen through the surface of SEM. The original honeycomb-like pores have almost all been covered by the sealing film, and the cross-sectional results show that the thickness of the sealing film is very large. The electrochemical impedance spectrum results showing only one capacitive reactance arc also indicate that at this time, both the porous film and the barrier film are covered by the sealing film, leaving only the double electric film and the charge transfer resistance at the interface between the sealing film and the sodium chloride solution.

Firstly, for the phosphate ion, it will react with the Al^{3+} produced by dissolution to form AlPO_4 . The reaction equation is as follows:



AlPO_4 has a strong adsorption capacity and can adhere to the inner walls of pores, reducing pore size and decreasing the mass of corrosive media in contact with

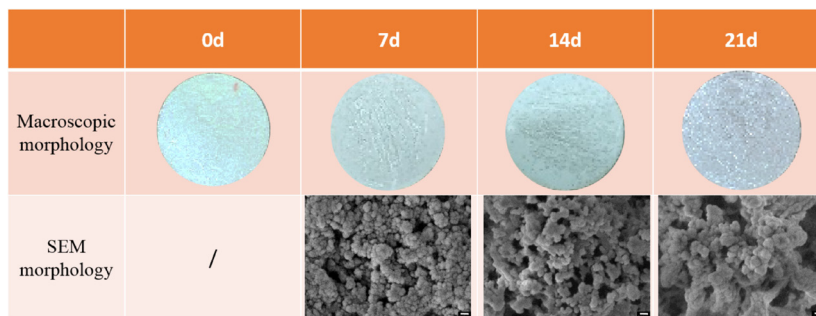


Figure 19. Comparison of the macroscopic morphology, SEM and mass loss test results of the immersion aging test.

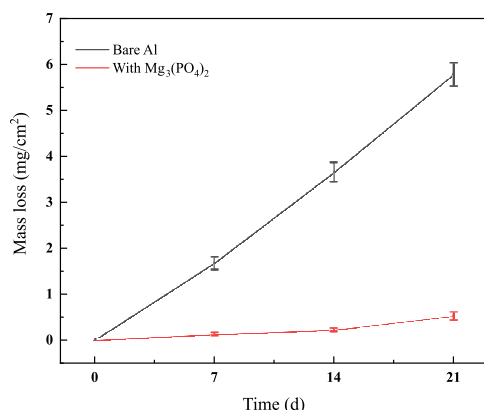


Figure 20. Comparison of weight loss *per* unit area between the bare substrate of 2024 aluminum alloy and anodic oxide film after adding magnesium phosphate.

the barrier film. As for magnesium ions, the process of sealing anodic oxidation pores is much more complex, during which the assistance of PO_4^{3-} and Al^{3+} is required. Magnesium ion sealing requires the creation of a medium-temperature and weak alkaline environment. However, the electrolyte temperature is different from the medium-temperature and is generally weakly acidic. Therefore, for a long time, the surface of aluminum alloy mainly undergoes anodic oxidation reactions.²⁵ As the dissolution rate of the anodic oxide film increases in the later stage and the surface porosity rises, the reaction on the anode begins to be dominated by the dissolution of the oxide film, that is:



The reaction between alumina and H^+ will consume H^+ near the anode area, causing the concentration of OH^- near the anodic oxide film to start increasing. In addition, since phosphoric acid is a weak acid, its acid radical ions will undergo hydrolysis reaction in the anode area, and the reaction equation is as follows:



The hydrolysis reaction will further increase the concentration of OH^- near the anode region. Meanwhile, the local temperature in the anode area will rise due to the Joule heat effect and electrochemical exothermic effect in the anodic oxidation process of aluminum alloys. The anodic oxidation time prolongs and the Joule heat effect becomes more obvious as the surface impedance of the aluminum alloy increases according to Joule's law: $Q = I^2Rt$. Therefore, the medium temperature and OH^- conditions required for magnesium ion sealing can

be locally achieved in the anode area. Moreover, due to the dissolution of aluminum oxide, H^+ is lost inside and near the pores, forming local electronegativity regions. It also drives Al^{3+} and Mg^{2+} into the interior of the pores and undergoes the following reactions with OH^- :



Both $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ can co-precipitate in the formation of pores, result in a role in sealing the pores. $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ can also generate MgO and Al_2O_3 after high-temperature drying, resulting in better sealing effect. Therefore, both phosphate ions and magnesium ions promote the sealing of anodic oxide film. The synergistic effect between phosphate ions and magnesium ions simultaneously are determined, and the presence of phosphate ions also helps to facilitate the sealing of magnesium ions.

Conclusions

Magnesium phosphate is added to electrolyte based on the traditional acidic electrolyte, aiming to further improve the corrosion resistance of anodic oxide film. The corrosion resistance is characterized by electrochemical and other testing methods, and the optimal process parameters are determined. Meanwhile, a more detailed study on anodic oxidation process mechanism of adding magnesium phosphate is conducted. The main research conclusion are as follows: (i) the anodic oxide film of 2024 aluminum alloy was prepared by the constant current method. Anodic oxide film with better corrosion resistance can be stably generated by changing the anodic oxidation parameters. The results show that the film prepared under the condition of an anodic oxidation current of 0.144 A cm^{-2} , an electrolyte temperature of 37°C , and an anodic oxidation time of 36 min demonstrate the best corrosion resistance; (ii) salt spray experiment and immersion aging experiment show that the structure of anodic oxide film cannot completely be destroyed after 14-day salt spray and 21-day immersion aging. The anodic oxide film with magnesium phosphate addition still show certain corrosion resistance. The electrochemical results show that the corrosion resistance of anodic oxide film with magnesium phosphate addition are superior to those of anodic oxide film without magnesium phosphate addition; (iii) both phosphate ions and magnesium ions promote the sealing of anodic oxide film. The synergistic effect between phosphate ions and magnesium ions simultaneously are determined, and the presence of phosphate ions also helps to facilitate the sealing of magnesium ions.

The growth, dissolution and sealing mechanism of anodic oxide film are indeed complex after the addition of magnesium phosphate. The mechanism which adding magnesium phosphate promotes the corrosion resistance of anodic oxide film is inferred based on the limited sealing agent composition, morphology, elemental composition, phase and electrochemical results in this research. The specific complex process still requires more experiments for verification. The detailed mechanism is also the focus of subsequent research.

Data Availability Statement

We declare that all the experimental data in this paper are obtained through experimental tests and have absolute authenticity. All relevant data are within the paper.

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Author Contributions

Mindi Deng was responsible for writing original draft, visualization, validation, methodology, investigation; Jinzhi Chen, Xu Zhou, Zhixiong Xie for experiment and characterization; Jie Min for supervision, resources, project administration, funding acquisition, formal analysis, data curation.

References

1. Rajan, N.; Sri, M. N. S.; Anusha, P.; Thanigaivelan, R.; Vijayakumar, S.; *Surf. Eng. Appl. Electrochem.* **2023**, *59*, 719. [Crossref]
2. Caliari, P. C.; Pacheco, M. J.; Ciríaco, L. F.; Lopes, A. M. C.; *J. Braz. Chem. Soc.* **2017**, *28*, 557. [Crossref]
3. Xu, J.; Song, Y.; He, K.; Zhang, H.; Dong, K.; Cai, Y.; Han, E.-H.; *Colloids Surf., A* **2024**, *703*, 135229. [Crossref]
4. Stephan, J.; Kasneryk, V.; Serdechnova, M.; Scharnagl, N.; Gazenbiller, E.; Vaghefinazari, B.; Volovitch, P.; Starykevich, M.; Blawert, C.; Zheludkevich, M. L.; *Appl. Surf. Sci.* **2024**, *659*, 159919. [Crossref]
5. Meng, Y.-B.; Li, S.-M.; Liu, J.-H.; Yu, M.; Tian, W.-M.; *Rare Met. (Beijing, China)* **2022**, *41*, 3865. [Crossref]
6. Aperador, W.; Aperador, J.; Orozco-Hernández, G.; *Metals* **2024**, *14*, 1462. [Crossref]
7. Xu, Z.; Cai, B.; Yan, L.; Pang, X.; Gao, K.; *Corros. Sci.* **2024**, *233*, 112077. [Crossref]
8. Mao, Y.; Zhu, Y.; Deng, C.-M.; Sun, S.; Xia, D.-H.; *Eng. Failure Anal.* **2022**, *142*, 106759. [Crossref]
9. Meng, Y.; Li, S.; Liu, J.; Yu, M.; Tian, W.; Chen, M.; *Corros. Sci.* **2020**, *170*, 108525. [Crossref]
10. Xia, Y.; Wu, L.; Yao, W.-h.; Hao, M.; Chen, J.; Zhang, C.; Wu, T.; Xie, Z.-h.; Song, J.-f.; Jiang, B.; Ma, Y.-l.; Pan, F.-s.; *Trans. Nonferrous Met. Soc. China* **2021**, *31*, 1612. [Crossref]
11. Palomino, L. E. M.; de Castro, J. F. W.; Aoki, I. V.; de Melo, H. G.; *J. Braz. Chem. Soc.* **2003**, *14*, 651. [Crossref]
12. Ferreira, D. S.; Pereira-Filho, E. R.; *J. Braz. Chem. Soc.* **2025**, *36*, e-20250130. [Crossref]
13. Mohammadi, M.; Yazdani, A.; Bahrololoom, M. E.; Alfantazi, A.; *J. Coat. Technol. Res.* **2013**, *10*, 219. [Crossref]
14. Vippola, M.; Vuoristo, P.; Lepistö, T.; Mäntylä, T.; *J. Mater. Sci. Lett.* **2003**, *22*, 463. [Crossref]
15. Miramontes, J. C.; Tiburcio, C. G.; Mata, E. G.; Alcála, M. Á. E.; Maldonado-Bandala, E.; Lara-Banda, M.; Nieves-Mendoza, D.; Olguín-Coca, J.; Zambrano-Robledo, P.; López-León, L. D.; Calderón, F. A.; *Materials* **2022**, *15*, 6401. [Crossref]
16. Çapraz, Ö. Ö.; Lundberg, K. E.; White, S. R.; Gewirth, A. A.; Sottos, N. R.; *Meet. Abstr.* **2018**, *MA2018-01*, 1956. [Crossref]
17. Daval, J.; Brunol, E.; Rouge, N.; Moutarlier, V.; Viennet, R.; Ricq, L.; Hihn, J.-Y.; *J. Electrochem. Soc.* **2025**, *172*, 013508. [Crossref]
18. Winter, L.; Lampke, T.; *Adv. Eng. Mater.* **2023**, *25*, 2300394. [Crossref]
19. Lee, S.; Cho, Y. J.; *Met. Mater. Int.* **2025**, *31*, 2598. [Crossref]
20. Zhang, C.; Chen, C.; Li, X.; Shao, Y.; Wang, Y.; Wang, J.; *J. Bio Tribo-Corros.* **2025**, *11*, 80. [Crossref]
21. Woldemedhin, M. T.; Raabe, D.; Hassel, A. W.; *Electrochim. Acta* **2012**, *82*, 324. [Crossref]
22. Medvedev, I. M.; Kuttyrev, A. E.; Krasnyk, E. V.; *Steel Transl.* **2024**, *54*, 446. [Crossref]
23. Jafarzadeh, K.; Ashlaghi, H. A.; Alizadeh, A.; Abbasi, H. M.; *Bull. Mater. Sci.* **2024**, *47*, 215. [Crossref]
24. Yin, D.; Demirev, P. A.; Hamann, T. R.; Lee, D. M.; Harman, M. R.; Cyrana, M. V.; Storck, S. M.; Kerechanin II, C. W.; Srinivasan, R.; *J. Mater. Sci.: Mater. Eng.* **2025**, *20*, 65. [Crossref]
25. Yang, S.; Wang, C.; Li, F.; Liu, N.; Shi, P.; Wang, B.; Sun, R.; *J. Alloys Compd.* **2022**, *909*, 164710. [Crossref]

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