Effects of Ce(NO₃)₃ concentration on microstructure and properties of plasma electrolytic oxidation layer on 6061 alloy

Jian Shang, Fu Liu, Gaoyang Gu and Lingyao Meng

1 School of Materials Science and Engineering, Liaoning University of Technology, Jinzhou 121001, People’s Republic of China
2 Shenyang Fortune Precision Equipment Limited Company Shen Yang, 110623, People’s Republic of China
E-mail: shangjian@lnut.edu.cn

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Abstract
Plasma electrolytic oxidation treatment of 6061 Al alloy was carried out in a sodium silicate and sodium hydroxide alkaline electrolyte containing different concentrations of cerium nitrate (Ce(NO₃)₃) under constant current mode. The effects of Ce(NO₃)₃ concentration on the roughness, cross section and surface morphology, composition and phase composition, adhesion force and corrosion resistance of the prepared layer were studied by means of true color microscope, scanning electron microscope, x-ray energy spectrometer, x-ray diffractometer, micrometer scratcher and electro-chemical workstation. The results show that with the increase of Ce(NO₃)₃ concentration in the electrolyte, the thickness of the plasma electrolytic oxidation layer increases gradually, and the micropores and cracks increase, and the roughness increases first and then decreases. The plasma electrolytic oxidation layers under different concentrations of Ce(NO₃)₃ are mainly composed of α-Al₂O₃, γ-Al₂O₃ and a small amount of Al₅SiO₅. The Ce element in the layer is mainly present in the form of a mixture of Ce(OH)₄, Ce₂O₂ and Ce₂O₃. The increase of Ce(NO₃)₃ concentration reduces the binding strength between the plasma electrolytic oxidation layer and the matrix, increases the self-corrosion potential, decreases the self-corrosion current, and weakens the corrosion resistance. The layer with a concentration of 0.25 g l⁻¹ Ce(NO₃)₃ has less micropores and cracks, and has the better compactness. The bonding strength between the layer and the substrate is 27 N, the corrosion current density is 3.42 × 10⁻⁹ A cm⁻² and corrosion potential is −0.72 V, the best bonding strength and corrosion resistance is presented.

1. Introduction
A high specific strength, easy processing and molding, and good electrical and thermal conductivity characterize 6061 Al alloys. However, the alloys have low hardness, poor wear and corrosion resistance, which limits their further applications [1]. To improve the surface strength and properties of Al alloys, researchers have used chemical oxidation [2], anodizing [3], laser cladding [4], electroplating [5], spraying [6], plasma electrolytic oxidation (PEO) [7, 8] and other methods. For surface modification, plasma electrolytic oxidation layer offered good wear resistance and corrosion resistance [9]. However, the micropores and cracks formed during the plasma electrolytic oxidation process will restrict their application in corrosive environments. Therefore, controlling the plasma electrolytic oxidation layer pores and improving the compactness require further study. Researchers have changed the electrolyte composition and treating parameters, such as adding nano-SiO₂, ZrO₂, SiC, TiO₂, Al₂O₃, Nb₂O₅, CeO₂, graphene and other particles into the electrolyte [10–17]. These particles in the electrolyte can increase the density of the prepared layer. However, adjustment and optimization were carried out by post-sealing treatment, such as hydration sealing, rare-earth sealing, inorganic salt sealing, and organic acid sealing [18–20]. Studies have shown that rare-earth sealing can effectively improve the corrosion resistance of the prepared layer. L. Pezzato [21], who studied the effect of La(NO₃)₃ on the plasma electrolytic oxidation layer of a 7075 Al alloy, found that the plasma electrolytic oxidation layer had high compactness and corrosion resistance.
resistance at a concentration of 0.05 g\ l^{-1}. The metal La was present in the form of La(OH)$_3$. Jun Peng Lu\cite{22} studied a Mg alloy pretreated with 0.06 mol\ l^{-1} Y(NO$_3$)$_3$, and found that plasma electrolytic oxidation had better corrosion resistance. The study determined that the rare-earth metals were deposited as Nd$_2$O$_3$ on the prepared layer surface and in the matrix. M. Toorani\cite{23} found that when the concentration of lanthanum nitrate was 0.5 g\ l^{-1}, the layer was the thickest, the density was the best, and the corrosion resistance was improved. In addition, rare-earth metal ions were present as La$_2$O$_3$. The researcher considered that the rare-earth metal ions promoted the suppression of the grain length and increased the thickness and compactness of the prepared layer; however, rare-earth oxides or hydroxides showed a good corrosion inhibition effect. Thus, the corrosion resistance of the prepared layer could be further improved\cite{24–27}. At present, research on the plasma electrolytic oxidation treatment in rare-earth-containing salts solutions were little and the influence mechanism of rare-earth cations on the microstructure and properties of the prepared layer was not clear. And then, by adding a larger concentration range (0.25–1.5 g\ l^{-1}) of cerium nitrate into the electrolyte to prepare the plasma electrolytic oxidation layer on the 6061 Al alloy were studied. Then, the effects of low to high concentrations of cerium nitrate on the thickness, roughness, morphology, phase composition and structure, as well as the adhesion and corrosion resistance of the prepared layers were investigated. Furthermore, the effect mechanism of the rare-earth cerium nitrate on the performance of the plasma electrolytic oxidation layer was discussed.

2. Experimental

2.1. Experimental materials

The source of materials and reagents used in present experiment is shown in table 1. The substrate used was a 6061 Al alloy sheet 15 × 15 × 4 mm in size, and the chemical composition of the sample in wt.% was: 0.2–0.4 Cu, 0.2 Mn, 0.8–1.2 Mg, 0.25 Zn, 0.04–0.3 Cr, 0.4–0.8 Si, 0.7 Fe, others, and Al balance. The samples were sanded with 600–1200 # sandpaper, ultrasonically cleaned with absolute ethanol, soaked in 50 g\ l^{-1} NaOH for 10 s, soaked in 2% HF and 20% HNO3 for 10 s, rinsed with a sufficient amount of deionized water, and then dried in air. The composition of the electrolyte was 2 g\ l^{-1} of NaOH, 10 g\ l^{-1} of Na$_2$SiO$_3$, and the concentrations of added Ce(NO$_3$)$_3$ were 0.25, 0.5, 1, and 1.5 g\ l^{-1}.

2.2. Experimental methods

The plasma electrolytic oxidation experiments were done through WHD-30 tester, which contained a power workstation to determine the corrosion resistance of the ceramic layer. The saturated calomel electrode served as the reference electrode, The platinum electrode is the auxiliary electrode, and the sample to be tested is the working electrode. The corrosive medium is 3.5% NaCl with the temperature is 25 °C. The scanning range is −1.5 to −0.3V, and the scanning speed is 0.5 mV s$^{-1}$ after 1 h immersion duration. EIS test frequency range is

### Table 1. Sources of materials and reagents used in experiment.

| Material and reagents | Purity of reagents | Source |
|-----------------------|--------------------|--------|
| HF                    | Analysis           | Sinopharm Group Chemical Reagent Co. |
| HNO$_3$               | Analysis           | Sinopharm Group Chemical Reagent Co. |
| Na$_2$SiO$_3$         | Analysis           | Sinopharm Group Chemical Reagent Co. |
| NaOH                  | Analysis           | Sinopharm Group Chemical Reagent Co. |
| Ce(NO$_3$)$_3$        | Analysis           | Sinopharm Group Chemical Reagent Co. |
| 6061 Al plates        |                    | Shanghai Haoshuan Metal Materials Co. |
0.01–100 000 Hz, the amplitude is 10 mV. The test results were fitted and analyzed by Origin, CView and ZSimpWin software.

3. Results and discussion

3.1. Surface three-dimensional appearance

Figure 1 shows the three-dimensional morphology of the prepared layer with different concentrations of Ce(NO₃)₃. As shown in the figure, the ceramic layer was undulating, where the maximum undulation height was 75.00 μm, as shown in figure 1(c), while the lowest undulation height was 50.00 μm, as shown in figure 1(a), and the undulations in figures 1(b) and (d) were 58.35 μm and 60.00 μm, respectively. As the concentration of Ce(NO₃)₃ additive increased, the undulation height of the ceramic layer increased; however, when it increased to 1.5 g l⁻¹, undulation decreased. The undulations of the ceramic layer were related to the breakdown discharge behavior. Under constant current mode, as the thickness of the ceramic layer increased, the breakdown discharge was more difficult, the discharge was uneven, and the single spark energy was large, It is induced that the ceramic layer to undulate unevenly. However, when the concentration of rare-earth Ce(NO₃)₃ was high, the number of discharge sparks increased, the single spark energy was small, and the ceramic layer was more uniform.

3.2. Surface roughness

Figure 2 shows the roughness parameters after plasma electrolytic oxidation of different concentrations of Ce(NO₃)₃, where Ra denotes the arithmetic mean roughness, Rp is the maximum peak height, Rv is the maximum valley peak height, Rz is the average peak-to-valley depth, and Rq is the root mean square roughness. The roughness values of Ra, Rp, Rv, Rz, and Rq initially increased and then decreased with increasing lanthanum nitrate concentration. The roughness was mainly determined by the degree of bulging of the discharge buildup product and the degree of dishing of the discharge micropores. The discharge buildup product showed a large influence. The addition of Ce(NO₃)₃ increased the conductivity of the electrolyte, and the number of anti-sparks increased, resulting in an increase in the number of accumulated products. Therefore, the roughness value increased with increasing roughness. When the concentration was very high, the rare-earth ions entered the discharge channel, promoting oxide nucleation in the micropores, forming a plurality of closed and semi-closed micropores, and reducing the porosity of the ceramic layer and reducing the roughness.
3.3. Surface topography

Figure 3 shows the scanning electron microscope surface morphology of the plasma electrolytic oxidation layer of different concentrations of Ce(NO$_3$)$_3$, where the elliptical small image in the figure shows a 2,000-fold magnification of the local area. As shown in Figure 3, the surface of the 6061 Al alloy after the addition of Ce(NO$_3$)$_3$ plasma electrolytic oxidation was rugged, with a crater-like shape that was convex, and the center has a horn-like micropore, surrounded by discharge-like fractal particles. As the concentration of cerium nitrate increased, the deposited product changed from a needle shape in Figure 3(a) to small spherical shape as shown in Figure 3(d). The accumulated products were continuously reduced, the cracks and micropores continuously increased, and the crater-like protrusions became larger, as shown in figures 3(c), (d). During the plasma electrolytic oxidation process, the spark discharges caused the surface of the substrate to become instantaneously high temperature ($10^3$–$10^4$K) [28]. Thus, molten alumina was ejected from the discharge channel and contacted...
the electrolyte, forming a crater shape, where the ejected alumina was solidified by the cold to form a solution particle. With increasing Ce(NO$_3$)$_3$ concentration, the conductivity of the electrolyte improved, the final stage of the reaction was more intense, and the energy of each spark was higher, forming larger craters and globular solution particles, while the high concentration of Ce(NO$_3$)$_3$ increased the surface thermal stress, which produced more cracks.

3.4. Surface composition and distribution

Figure 4 shows the composition of the ceramic layer after plasma electrolytic oxidation of different concentrations of Ce(NO$_3$)$_3$: (a) 0.25 g l$^{-1}$, (b) 1.5 g l$^{-1}$.

![Figure 4. Composition and composition of PEO layer with different concentrations of Ce(NO$_3$)$_3$: (a) 0.25 g l$^{-1}$, (b) 1.5 g l$^{-1}$.](image)

3.5. Cross-section and composition

Figure 5 shows the cross-sectional morphology and energy spectrum of the different concentrations of Ce(NO$_3$)$_3$ in the 6061 Al alloy after plasma electrolytic oxidation. As shown in figure 5(a), there were no obvious boundaries between the loose and dense layers, and there were many small holes in the ceramic layer, where the
Figure 5. Cross-section morphology and energy spectrum of PEO layer with different concentrations of Ce(NO₃)₃: (a) 0.25 g l⁻¹, (b) 0.5 g l⁻¹, (c) 1 g l⁻¹, (d) 1.5 g l⁻¹.
formation of holes was due to the breakdown discharge of the Al alloy. The high temperatures generated by the discharge melted the surface of the substrate to form a molten pool. The formation of the oxide layer consisted of an infinite cycle of melting, oxidation, and solidification. The voids in figures 5(b) and (c) were obviously enlarged, and the voids were connected to each other, while the voids were concentrated on the surface loose layer. As the concentration of Ce(NO₃)₃ increased, plasma electrolytic oxidation was severe, and the voids in the oxide layer increased. As clearly shown in figure 5(d), the oxide layer was very dense, where the density layer and loose layer were clearly defined, and the thickness of the ceramic layer increased. As shown by the energy spectrum, the ceramic layer contained elements such as Al, O, and Si. Plasma electrolytic oxidation of the Al alloy determined that there were Al and O elements in the ceramic layer. The Si elements were concentrated in the loose outer layer because the surface-melted alumina reacted with Si⁴⁺ in the electrolyte during the breakdown discharge. An additional portion of Si⁺⁺ entered the discharge channel and remained in the ceramic layer as the alumina solidified.

3.6. Phase composition
Figure 6 shows the XRD pattern of the ceramic layer prepared by plasma electrolytic oxidation with different concentrations of Ce(NO₃)₃. As shown in the figure, the ceramic layer was mainly composed of α-Al₂O₃ and γ-Al₂O₃, with more γ-Al₂O₃ loose layer, while the α-Al₂O₃ layer was less dense than Al₂SiO₅. The matrix Al also had a strong diffraction peak, which was mainly due to the fact that the x-rays penetrated the surface loose layer and reached the matrix. No Ce elements were detected in the ceramic layer, indicating that Ce(NO₃)₃ did not participate in the chemical reaction, and only provided the medium for the reaction, as the Ce of strontium was small, where the XRD detection limit was not reached. The oxide layer prepared by different concentrations of Ce(NO₃)₃ showed almost no changes in the content, indicating the phase composition of the unaltered ceramic layer of Ce(NO₃)₃ concentration.

3.7. Chemical composition
Figure 7 shows the full and resolution spectra of the surface of the plasma electrolytic oxidation layer with different concentrations of Ce(NO₃)₃. According to the map in 7(a), the surface of the ceramic layer contained elements such as Mg, Na, Ce, O, Si, and Al. The 7(c) Mg²⁺ peak with an Mg1s binding energy of 1304 eV was consistent with the peak of MgAl₂O₄, while the 7(d) peak for the Si₂p binding energy of 102.7 eV was consistent with the peak of Al₂OSiO₄. The binding energy of 7(e) Al₂p was 74.2 eV, while 73.8 eV was consistent with the binding energy of Al₂O₃, and the binding energy of 7(f) O1s was 532 eV [29, 30].

The general Ce3d high-resolution XPS spectrum contained three characteristic regions, namely the Ce3d₅/₂ region of 880–890 eV, the Ce3d₃/₂ and Ce3d₅/₂混合 region of 890–910 eV, and the 917 eV binding energy was the Ce3d₃/₂ satellite peak [31]. As shown in the high-resolution XPS spectrum of Ce3d in figure 7(b), there were also 3 characteristic peaks, namely, Ce3d₅/₂ of 882.7–885.8 eV, Ce3d₃/₂ and Ce3d₅/₂混合 areas of 899.5–903.7 eV, and a satellite peak of 916.7 eV. We determined from the position of the binding energy peak that Ce in the ceramic layer was composed of a mixture of Ce(OH)₃, Ce₂O₃, and Ce₂O₅.

In the electrolyte, the saturated solubilities of Ce(OH)₃ and Ce(OH)₄ were 4.9 × 10⁻⁶ and 9.5 × 10⁻¹¹, respectively, which promoted the formation of Ce(OH)₄ at a high pH value. After plasma electrolytic oxidation,
the electrolyte changed from colorless to yellow, which confirmed that Ce(OH)$_4$ precipitated, according to $\text{Ce}^{3+} + e^- \rightarrow \text{Ce}^{4+}$, $\text{Ce}^{4+} + 4\text{OH}^- \rightarrow \text{Ce}(	ext{OH})_4$. The instability of Ce(OH)$_3$ and Ce(OH)$_4$ in the high-temperature environment of the substrate surface easily converted into a stable oxide, according to $2\text{Ce(OH)}_3 \rightarrow \text{Ce}_2\text{O}_3 + 3\text{H}_2\text{O}$, and $\text{Ce(OH)}_4 \rightarrow \text{CeO}_2 + 2\text{H}_2\text{O}$ Under the action of an electric field, the anode material generated sparks, the water was decomposed and released oxygen $\text{[32]}$. Under the action of a strong electric field, oxygen would ionize $\text{O}^{2-}$ and move toward the substrate. In addition, $\text{Ce}^{3+}$ and $\text{Ce}^{4+}$ adsorbed on the surface of the anode and formed O$_2$ contacts with the oxides, and Ce$_2$O$_3$ was unstable and easily oxidized to CeO$_2$. The reaction formulas were:

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$$
$$2\text{Ce}^{3+} + 3\text{O}^{2-} \rightarrow \text{Ce}_2\text{O}_3$$
$$\text{Ce}^{4+} + 2\text{O}^{2-} \rightarrow \text{CeO}_2$$
$$2\text{CeO}_3 + \text{O}_2 \rightarrow 4\text{CeO}_2$$

3.8. Binding force

Figure 8 shows a graph of the acoustic emission and friction signals of the micro-scratch experiments after plasma electrolytic oxidation of the different concentrations of cerium nitrate. The real-time normal load that
first selected the sudden change in the acoustic emission signal was the critical load of ceramic layer combined failure. However, due to the surface quality of the substrate, the ceramic particles in the ceramic layer, along with the voids in the ceramic layer, showed that some interference signals existed during the scratch test [33]. From the scratch signals of the cerium nitrate additive in figures 8(a)–(d), the critical load values for the failure of the ceramic layer to the matrix were 27, 14.1, 15.4, and 21.5 N, respectively. According to the critical load of the combined failure, we determined that the Ce(NO$_3$)$_3$ additive with the lowest concentration of 0.25 g l$^{-1}$ had good sample adhesion after plasma electrolytic oxidation. The frictional signal increased linearly with increasing load, and as the acoustic signal appeared, the frictional force bounced downward. Part of the ceramic layer was destroyed, and the scratched needle touched the Al alloy substrate; however, the surface of the plasma electrolytic oxidation layer was uneven, the surface had crystalline products, the roughness was large, and there were many fine micropores in the ceramic layer with cracks that had a large effect on the friction and acoustic emission signals. Therefore, many beating signals appeared in the figure.

### 3.9. Potentiodynamic polarization tests

Figure 9 shows the polarization curve of the ceramic layer after plasma electrolytic oxidation of different concentrations of Ce(NO$_3$)$_3$. As shown in the figure, the ceramic layers after different concentrations of Ce(NO$_3$)$_3$ plasma electrolytic oxidation treatment had a passivation zone, with passivation intervals between $-1.2$ and $-0.7$ V. When the surface of the working electrode had an insulating coating, the actual corrosion site was mainly concentrated at the interface between the coating and the substrate. The corrosion resistance of the coating material was mainly dependent on the physical shielding effect of the insulating coating on the corrosive medium. The large passivation zone of the ceramic layer after plasma electrolytic oxidation was due to the ceramic layer Al$_2$O$_3$ grown in situ on the Al substrate, and the inner layer $\alpha$-Al$_2$O$_3$ showed good compactness and tight adhesion to the matrix, which was good for the Cl$^-$ ion shielding effect [34]. The passivation zones of the plasma electrolytic oxidation ceramic layers of 0.25 and 0.5 g l$^{-1}$ Ce(NO$_3$)$_3$ were slightly larger than the ceramic layers of Ce(NO$_3$)$_3$ of 1 and 1.5 g l$^{-1}$. It indicated that the density of plasma electrolytic oxidation layer was reduced with an increase in Ce(NO$_3$)$_3$ concentration. This corresponded to the surface and cross-sectional morphologies of figures 3(d) and 5(d), which resulted in the penetration and contact of the corrosive medium along the pores into the substrate, and the corrosion resistance was affected.

Table 2 shows the parameters of the potentiodynamic polarization curves with different concentrations of the Ce(NO$_3$)$_3$ plasma electrolytic oxidation layer. As shown in table 1, as the concentration of Ce(NO$_3$)$_3$
increased, the corrosion potential of the plasma electrolytic oxidation gradually decreased. The corrosion potential of the plasma electrolytic oxidation layer at a concentration of 0.25 g l$^{-1}$ Ce(NO$_3$)$_3$ was the highest, indicating that the plasma electrolytic oxidation layer had a relatively low corrosion tendency. As the concentration of Ce(NO$_3$)$_3$ increased, the corrosion current of the plasma electrolytic oxidation layer gradually increased. The 0.25 g l$^{-1}$ Ce(NO$_3$)$_3$ concentration plasma electrolytic oxidation layer had the lowest corrosion current density, indicating that the plasma electrolytic oxidation layer had a relatively slow corrosion process. In general, the higher the corrosion potential, the smaller the corrosion current, and the better the corrosion resistance[10]. Therefore, the ceramic layer after 0.25 g l$^{-1}$ Ce(NO$_3$)$_3$ plasma electrolytic oxidation showed the best corrosion resistance, and different concentrations of Ce(NO$_3$)$_3$ changed the compactness of the ceramic layer, resulting in a difference in corrosion resistance.

### 3.10. Electrochemical impedance spectroscopy

Figure 10 shows the Nyquist and Bode spectra of the Al alloy in 3.5% NaCl solution after the plasma electrolytic oxidation of different concentrations of Ce(NO$_3$)$_3$. As shown in the Nyquist diagram, the radius of the capacitive reactance initially decreased and then increased with increasing Ce(NO$_3$)$_3$ concentration. The 0.25 g l$^{-1}$ Ce(NO$_3$)$_3$ plasma electrolytic oxidation ceramic layer had the largest arc resistance radius and it is indicated that the ceramic layer with 0.25 g l$^{-1}$ Ce(NO$_3$)$_3$ concentration had the best corrosion resistance. Typical Warburg diffusion occurred in the low-frequency region of the Nyquist diagram, and corrosion at the interface between the oxide film and the substrate intensified. Corrosion products accumulated in the oxide film voids, and the rate of corrosion product formation was greater than the diffusion rate. The high-frequency and low-frequency zones of the Bode diagram represented the time constants of the plasma electrolytic oxidation loose and dense layers, respectively, where the initial phase angle was very high, indicating that the loose layer had a good shielding effect on the corrosive medium. The highest phase angle of 0.25 g l$^{-1}$ Ce(NO$_3$)$_3$ was located in the low-frequency region, which the low-frequency impedance mode |Z| maximum indicated the best corrosion resistance.

In the equivalent circuit diagram shown in figure 11, Rs denotes the solution resistance, R$_1$ and R$_2$ are the loose layer resistance and the dense layer resistance, respectively, CPE$_1$ and CPE$_2$ denote the loose layer capacitance and the dense layer capacitance, R$_t$ is the charge transfer resistance, and W denotes Warburg impedance. Table 3 shows the equivalent circuit data after the PEO of different concentrations of Ce(NO$_3$)$_3$. According to R$_1$ and R$_2$ in table 3, as the concentration of Ce(NO$_3$)$_3$ increased, the resistance value decreased, and R1 and R2 of 0.25 g l$^{-1}$ Ce(NO$_3$)$_3$ were the highest; thus, the 0.25 g l$^{-1}$ Ce(NO$_3$)$_3$ ceramic could be determined, and the layer had the best corrosion resistance with the best compactness.

#### Table 2. Electrochemical parameters of PEO layer with different concentrations of Ce(NO$_3$)$_3$.

| Concentration (g l$^{-1}$) | 0.25 | 0.5 | 1 | 1.5 |
|---------------------------|------|-----|---|----|
| corrosion potential (V)   | −0.69996 | −0.71377 | −0.70619 | −0.7322 |
| corrosion current density (A cm$^{-2}$) | 9.68 × 10$^{-9}$ | 3.42 × 10$^{-8}$ | 6.52 × 10$^{-7}$ | 2.49 × 10$^{-8}$ |

![Figure 9. Potentiodynamic polarization curve of PEO layer with different concentrations of Ce(NO$_3$)$_3$.](image-url)

![Figure 10. Nyquist and Bode spectra of Al alloy in 3.5% NaCl solution after PEO with different concentrations of Ce(NO$_3$)$_3$.](image-url)

![Figure 11. Equivalent circuit diagram of Al alloy after PEO with different concentrations of Ce(NO$_3$)$_3$.](image-url)
The capacitive behavior of the film layer and the matrix could be better simulated by the CPE component, where the CPE was comprised of a constant phase angle component related to the natural oxide film. The impedance formula of the CPE could be expressed by [35]:

![Figure 10](https://example.com/image10.png) Shows the Nyquist and Bode spectrum after PEO layer with different concentrations of Ce(NO₃)₃.

![Figure 11](https://example.com/image11.png) Is a fitting equivalent circuit diagram of electrochemical impedance spectroscopy.

The capacitive behavior of the film layer and the matrix could be better simulated by the CPE component, where the CPE was comprised of a constant phase angle component related to the natural oxide film. The impedance formula of the CPE could be expressed by [35]:
### Table 3. Equivalent circuit data after PEO layer with different concentrations of Ce(NO₃)₃

| Sample | 0.25g L⁻¹ Ce(NO₃)₃ | 0.5g L⁻¹ Ce(NO₃)₃ | 1g L⁻¹ Ce(NO₃)₃ | 1.5g L⁻¹ Ce(NO₃)₃ |
|--------|--------------------|--------------------|-----------------|-----------------|
| Rₛ(Ω·cm²) | 29.65 | 24.52 | 23.45 | 28.06 |
| Yₒ₁(Ω⁻¹·cm⁻²·sⁿ) | 3.20 × 10⁻⁶ | 2.75 × 10⁻⁶ | 1.24 × 10⁻⁶ | 1.03 × 10⁻⁶ |
| n₁ | 0.70 | 0.73 | 0.68 | 0.60 |
| Rᵯ(Ω·cm²) | 266.5 | 100 | 31.9 | 121.4 |
| Yₒ₂(Ω⁻¹·cm⁻²·sⁿ) | 1.43 × 10⁻⁶ | 1.25 × 10⁻⁶ | 6.75 × 10⁻⁶ | 1.49 × 10⁻⁶ |
| n₂ | 0.91 | 0.87 | 0.68 | 0.89 |
| Rᵯ(Ω·cm²) | 122400 | 80500 | 31300 | 78100 |
| Yₒ₃(Ω⁻¹·cm⁻²·sⁿ) | 2.21 × 10⁻⁵ | 4.95 × 10⁻⁵ | 5.32 × 10⁻⁵ | 5.79 × 10⁻⁵ |
| n₃ | 0.66 | 0.56 | 0.58 | 0.63 |
| Rᵯ(Ω·cm²) | 231.0 | 218.4 | 254.7 | 192.4 |
| W | 3.88 × 10⁻⁵ | 3.92 × 10⁻⁵ | 4.55 × 10⁻⁵ | 4.39 × 10⁻⁵ |

**Figure 12.** Schematic diagram of corrosion mechanism of PEO layer.
where $j$ is an imaginary unit ($j^2 = -1$), $\omega$ is the angular frequency ($\omega = 2\pi f$), $Q$ is a constant phase element, and $n$ ($0 < n \leq 1$) is an empirical exponent that could vary between a perfect resistor and a perfect capacitor [21].

3.11. Corrosion resistance mechanism

On the basis of the above experiments, a corrosion trend model was established, as shown in figure 12. The etching solution consisted of 3.5% NaCl, which had strong penetrability and a destructive effect on the oxide layer. As shown in figure 12(a), Cl ions penetrated the oxide layer to provide a conductive medium for electrochemical reactions. The reduction reaction of the platinum plate cathode followed

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \uparrow,$$

and the oxygen evolution reaction followed

$$O_2 + 2H^+ + 4e^- \rightarrow 2H_2O.$$

At the same time, the plasma electrolytic oxidation of the sample anode oxidation reaction followed

$$Al \rightarrow Al^{3+} + 3e^-,$$

as shown in figures 12(c) and (d). As corrosion progressed, corrosion products were deposited at the micropores and cracks in the layer, preventing the progression of the $Al^{3+} + 3OH^- \rightarrow Al(OH)_3$ reaction.

Rare-earth oxides CeO$_2$ and Ce$_2$O$_3$ in the ceramic coating did not participate in the reaction, but had a good shielding effect on the corrosive medium and prevented the corrosive medium from entering the matrix. The compactness of the ceramic layer was the decisive factor that affected the corrosion resistance. The addition of a suitable concentration of Ce(NO$_3$)$_3$ in the electrolyte could also significantly increase the thickness and compactness of the ceramic layer [36, 37].

4. Conclusions

With increasing Ce(NO$_3$)$_3$ concentration, the thickness of the ceramic layer increased gradually, micropores and cracks increased, and the roughness initially increased and then decreased. The ceramic layer was mainly composed of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$, and a small amount of Al$_2$SiO$_5$. Ce, which mainly existed in the form of a mixture of Ce(OH)$_3$, CeO$_2$, and Ce$_2$O$_3$, was concentrated in the concave structure. With increasing Ce(NO$_3$)$_3$ concentration, the bonding strength between the ceramic layer and the matrix decreased, where the binding bonding strength of 0.25 g l$^{-1}$ lanthanum nitrate additive was 27 N. The corrosion resistance of the ceramic layer decreased with increasing Ce(NO$_3$)$_3$ concentration, resulting in better corrosion resistance of the 0.25 g l$^{-1}$ lanthanum nitrate.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Jian Shang https://orcid.org/0000-0001-5135-6574

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