Evaluation of anticorrosive and self-healing performances of TiO$_2$-added cerium conversion coatings developed on 211Z aluminium alloy

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Abstract

Titanium dioxide (TiO$_2$) sol was added to the cerium conversion coating (CeCC) for preparing the CeCC-TiO$_2$ composite coating covered on the surface of 211Z aluminium alloy. The anticorrosive and self-healing performances of the composite coatings were further investigated. The result shows the increasing $E_{g}$ of CeCC-TiO$_2$ could improve the anticorrosive and anti-intergranular corrosion performances of 211Z aluminium alloy under NaCl solution. Because the composite coating with high $E_{g}$ value can effectively suppress the anodic reactions, provide greater coating resistance, and bring more compact surface structure. The self-healing ability of CeCC could be improved by adding TiO$_2$ sol and the $E_{g}$ value of the CeCC-TiO$_2$ composite coating with the best self-healing performance is 3.38 eV. The cause of it lies in that the coefficient of the dynamic inhibition of Ce$^{3+}$ and the inert inhibition of Ce$^{4+}$ influences the self-healing performance of the composite coatings.

1. Introduction

Existing studies have shown that the cerium conversion coating (CeCC) deposited on the alloy surface could enhance the anti-corrosion performance, because CeCC has excellent corrosion resistance [1], paint adhesion [2], self-healing [3], and more environmental friendly performance than chromate conversion coating [4]. In our previous investigation [3], the band gap ($E_{g}$) of CeCC can be adjusted by the addition of TiO$_2$ sol during the CeCC formation process, its value is 3.07 eV, 3.38 eV and 3.51 eV when the adding content of TiO$_2$ sol is 0 ml, 0.5 ml and 1.5 ml, respectively.

Till now, there have some studies on the functional application for the cerium-based oxides by adjusting $E_{g}$ values [6–9]. But it did not attract much attention on the corrosion resistance of CeCC with different $E_{g}$ values. 211Z aluminium (Al-Cu-Mn series) is a kind of high strength, toughness and heat resistant aluminium alloy, in which the presence of copper alloying elements renders the alloy susceptible to pitting/intergranular corrosion [10]. This paper intends to improve the anticorrosive performance of 211Z aluminium alloy by covered with a CeCC-TiO$_2$ composite coating and pay attention to the influence of adjustable $E_{g}$ value on the anticorrosive and self-healing performances of as-prepared composite coating. During the preparation process of CeCC based on 211Z aluminium alloy, TiO$_2$ sol was added to get the CeCC-TiO$_2$ composite coating with tunable bandgap by dipping method as the same in [5].

2. Experiment

2.1. Coatings preparation

The schematic representation of the experimental setup is shown in figure 1. Firstly, TiO$_2$ sol was prepared. Diethanolamine (4.5 mL) as a stabilizer was added in the mixed solution of Ti(OFBu)$_4$ (11.0 mL) and ethanol.
(56 mL), and then deionized water (0.7 mL) and ethanol (7.2 mL) were dropwise put into it to obtain the TiO2 sol.

Next, the composite coating was prepared on 211Z aluminium alloy substrates by dipping method. Configured 50 mL Ce(NO₃)₃·6H₂O (0.046 mol L⁻¹, pH = 2.2) solution and adjusted the temperature to 60 °C, added 0.5 mL H₂O₂ (30%) into the solution followed by placing the pretreated 211Z substrate sample, then added TiO₂ sol (The content is 0 mL, 0.5 mL and 1.5 mL, respectively in the investigation) into the solution accompanied by ultrasonic treatment. After ten minutes, washed the coated sample three times by using deionized water.

Finally, the coated sample was soaked in Na₃PO₄ (0.066 mol L⁻¹, pH = 4.5) solution at 85 °C for 5 min. After natural drying for one day, the coated sample was calcined at 500 °C for 1 h in the muffle furnace.

2.2. Characterization and measurement
Open circuit potential (OCP), potentiodynamic polarization curve and electrochemical impedance spectroscopy (EIS) were carried out on the electrochemical workstation (CHI660E) to estimate the electrochemical parameters of as-prepared samples in 3.5 wt% NaCl solution at room temperature. All the samples made for electrochemical measurement were used as a working electrode, and 1 cm² was exposed as a working area. In addition, the platinum foil was worked as a counter electrode and the saturated calomel electrode was played as a reference electrode in a typical three-electrode system. The measure of OCP was kept for 400 s over the range from −1.0 V to 1.0 V. The polarization curve test result was obtained by sweeping the potential at a scan rate of 10 mV s⁻¹ in the voltage range from −1.4 V to 0.2 V. A frequency swept from 10⁵ Hz to 10⁻² Hz and a scan rate of 10 mV s⁻¹ were utilized for the EIS measurement.

The intergranular corrosion experiments were carried out on the bare 211Z aluminium alloy and the coated 211Z aluminium alloy with CeCC-TiO₂ composite coating according to ASTM G100-92. The sample for this experiment was a cylinder with a length of 40 mm and a diameter of 12 mm. The measured sample should be completely submerged in the corrosion solution (57 g L⁻¹ NaCl + 10 mL L⁻¹ H₂O₂) at 30 ± 3 °C for 6 h. Then the corroded products were removed, and the sample was washed with deionized water. The maximum depth of intergranular corrosion was observed by metallographic microscope (4XC-V).

The self-healing test was carried out as follows. After drawing a cross grid with a width of 20 ∼ 40 μm on the surface of the coated samples, the scratch samples were then immersed in 3.5 wt%NaCl solution for a certain number of days and measured the OCP. The scratch morphology was observed by scanning electron microscope (SEM SU8010) equipped with EDX. Through measuring OCP and observing the scratch morphology, the self-healing performance could be characterized.

3. Results and discussion

3.1. Anticorrosion performance
In our former investigation [5], the introduction of TiO₂ into conventional CeCC resulted in an obvious change of band gap. For different contents of TiO₂ sol addition shown as 0 mL, 0.5 mL and 1.5 mL, the Eg values are 3.07 eV, 3.38 eV and 3.51 eV, respectively. So, in the investigations, we prepared the CeCC-TiO₂ composite coatings on the 211Z aluminium alloy substrate with different TiO₂ sol content, which is 0 mL, 0.5 mL and 1.5 mL, respectively.
The polarization curves and EIS results of 211Z aluminium alloy covered by CeCC-TiO2 composite coatings with adjustable Eg values are shown in figure 2. The fitting results of parameters are listed in tables 1 and 2, respectively.

The corrosion potential is shifted from −1.207 V of the bare 211Z aluminium alloy to −0.795 V, −0.749 V and −0.641 V of the 211Z aluminium alloy covered by CeCC-TiO2 composite coatings with Eg values of 3.07 eV, 3.38 eV and 3.51 eV, respectively (table 1). Correspondingly, current density is diminished from 3.04 μA cm⁻² to 2.661 μA cm⁻², 2.342 μA cm⁻² and 1.140 μA cm⁻², respectively. Compared with the bare 211Z aluminium alloy sample, the cathode slope values of the polarization curve of the coated samples are reduced and anode slope values increase by a wide margin, which indicates that the anti-corrosive mechanism is the inhibition of the anodic reaction [11].

The above measured results showed that the anti-corrosion performance increases with the increase of Eg values of the CeCC-TiO2 composite coatings.

In figure 2(b), Rs is the solution resistance; R1 is the coating resistance. CPE is a constant phase angle element. When n is equal to 0, CPE is the resistance. When n is between 0 and 1, CPE is the capacitance [12].

It can be observed from the table 2 that the 211Z aluminium alloy covered by CeCC-TiO2 composite coatings with Eg values of 3.07 eV, 3.38 eV and 3.51 eV, has the coating resistance values (R1) of 507.4 ohm, 544.7 ohm and 551.3 ohm, respectively. In other words, with the increase of Eg values, R1 increases, which means the barrier effect of the coating layer is enhanced. The CPE values are related to the formation of electric double layer capacitance at aluminium surface [12], which is in the same order of magnitude (10⁻⁴) in table 2, with a little difference. In addition, n value is between 0 and 1, indicating that the electrode surface is not uniform during the test and the coating capacitance produces dispersion effect. The value of n is closer to 1, means the surface structure of electrodes is more compact [12]. All the value of n in table 2 is above 0.8, close to 1, indicating that the introduction of TiO2 can make the surface of CeCC coating more compact. It has a good effect on sealing electrode surface.

### Table 1. Electrochemical polarization parameters obtained from polarization curves.

| Eg/eV | \( E_{corr}/V \) | \( I_{corr}/\mu A \cdot cm^{-2} \) | Cathodic slope/1 × V⁻¹ | Anodic slope/1 × V⁻¹ |
|-------|------------------|-----------------|---------------------|---------------------|
| −(Blank) | −1.207 | 3.040 | 7.305 | 4.216 |
| 3.07 | −0.795 | 2.661 | 3.795 | 23.854 |
| 3.38 | −0.749 | 2.342 | 4.107 | 23.317 |
| 3.51 | −0.641 | 1.140 | 3.187 | 29.563 |

### Table 2. Fitting results of EIS in figure 2(b).

| Eg/eV | Rs/ohm | CPE/×10⁻⁴ | n | R1/ohm |
|-------|--------|------------|---|--------|
| 3.07 | 8.800 | 2.981 | 0.805 | 507.4 |
| 3.38 | 8.619 | 2.609 | 0.814 | 544.7 |
| 3.51 | 9.046 | 2.829 | 0.847 | 551.3 |
3.2. Anti-intercrystalline corrosion performance

Due to the high content of Cu in 211Z aluminum alloy, the intercrystalline corrosion is easy to occur. chloride ions are aggressive and would pass through and destroy the Al$_2$O$_3$ film of aluminium alloy, which would cause the partial dissolution of aluminium hydroxide and form small cracks.

Figure 3 shows the metallographic cross-sections of the uncoated/coated 211Z aluminium alloy with CeCC – TiO$_2$ composite coatings of different $E_g$ values after exposing in NaCl + H$_2$O$_2$ solution for 6 h. The intergranular corrosion depth was measured and calculated by scale according to ASTM G100-92. The intergranular corrosion depth of the uncoated sample is about $89\mu m$. For the coated samples, the intergranular corrosion depth decreases with the increase of $E_g$ values, which is $72\mu m$, $64\mu m$ and $61\mu m$, corresponding to $E_g$ values of 3.07 eV, 3.38 eV and 3.51 eV, respectively. The reason can be explained as follows. From table 2, with the increase of $E_g$ values, value of $n$ increases, which indicates that the coatings become more compact. Thus, the ability to block the passage of chloride ions through the coating is improved. As a result, the excellent shielding effect against chloride ions passing through the CeCC–TiO$_2$ composite coatings can effectively reduce the intergranular corrosion depth and improve the anti-intergranular corrosion performance of 211Z aluminium alloy.

3.3. Self-healing performance

There has been a self-healing mechanism of CeCC proposed by some researchers [13, 14]. It could be concluded that, under the action of chloride ions, CeCC could provide dynamic protection for the Al substrate by forming Ce-Al-O layer through the Ce$^{3+}$/Ce$^{4+}$ redox reaction at the defects, which could set more barriers against chloride ions passing through the coatings.

The open-circuit potential can reflect the corrosion tendency of the samples and characterize the anticorrosion performances. During the test, there is no current so that it could avoid the damage of the coating surface and reduce the influence on the following procedure. Therefore, the OCP test can be used as an electrochemical characterization method for self-healing performance. As can be seen from figure 4(a), the OCP values fluctuate with the prolongation of the immersion time and finally increase to $-0.2$ V after immersed for 60d. The variation of OCP value versus immersion time approximately reflects the change process of coating surface from destroyed to forming a new coating. At first, the scratched coating couldn’t protect the surface, so the corrosion tendency is increasing, the OCP value decreases. In the following time, the fluctuation of OCP value implies the repeated formation and damage of the newly generated coating. When the immersion time is long enough (60d), the scratched area on the exposed electrode surface could eventually form a complete new
coating, so it leads to the positive shift of the OCP value to −0.2 V. Figure 4(b) indicates the OCP values of 211Z aluminium alloy coated by CeCC-TiO₂ composite coatings with different Eg values when immersed for 0d, 5d, 10d, 30d, 55d and 60d in NaCl solution, respectively.

OCP values do not change significantly with the increase of the Eg values when the immersion time is not greater than 30d. However, when the immersion time is from 55d to 60d, the OCP values increase firstly and then decrease with the increase of the Eg values. The best self-healing Eg value of the CeCC-TiO₂ composite coating is 3.38 eV.

The possible reasons for this phenomenon are as follows. On the one hand, the increase of the Eg values makes n value increase (table 2), implying that denser surface of the coating can be gained with higher Eg values [12]. On the other hand, refer to our previous research results [5], with the increase of addition content of TiO₂ sol into the CeCC, the content of Ce³⁺ ions (transformed from Ce⁴⁺ ions) in the composite coating increases. These Ce³⁺ ions should form more insoluble cerium compounds. These compounds are redeposited on the scratched surface and inhibit the corrosion process in the surface of the aluminum alloy [15]. However, Ce⁴⁺ also has a good chemical inertia and low electronic conductivity so that it can effectively inhibit the transfer of charge and is beneficial to the inhibition of corrosion reaction [16], so the increase of Ce³⁺ means the decrease of Ce⁴⁺ in the composite coatings, which also reduces the capability of retarding corrosion by Ce⁴⁺. As a result of the coordination of the above two factors, when the Eg values are increased from 3.38 eV to 3.51 eV, the effect of dynamic inhibition caused by higher-proportioned Ce³⁺ is not greater than the effect of the inert inhibition of decreased proportion of Ce⁴⁺, so the ability against corrosion reaction of the composite coating may be reduced when the Eg value is up to 3.51 eV.

In order to observe the self-healing process, one CeCC-TiO₂ sample (Eg = 3.38 eV) with cross scratches was soaked in 3.5 wt% NaCl solution, at different soaked time (0d, 5d, 10d, 30d, and 60d, respectively), the sample was took out and observed the morphology of the same location of scratches, and then the sample was still soaked in the 3.5 wt% NaCl solution for the next observation. The morphological evolution of the scratched area is displayed in figures 5(a) to (f), respectively, the scratched area is marked with red dotted lines. With the prolongation of the immersion time, new substances are formed continuously at the scratched surfaces, and the scratches’ depths become shallower (From figures 5(a) to (d)). When the soaked time is up to 60d, the scratches are difficult to be identified (figure 5(e)). A same rectangular central area of scratches (Spectrum1 in figure 5(a) and Spectrum2 in figure 5(e)) was selected to assess the element composition of the scratches at different soaked time, the corresponding element composition is shown in figures 5(f) and (g), respectively. The scratches were deep enough to the substrate in figure 5(a), which means the composite coating on the scratched surface was completely removed before immersion (0d), so the substrate elements of Al, Cu and Mn are presented in figure 5(f). However, figure 5(g) shows there found Al, Cu, Mn and Ce elements in the EDS results of Spectrum2 area in the scratches of sample soaked in 3.5 wt% NaCl for 60d, which indirectly proves the self-healing capability of the composite coatings.

In summary, The CeCC-TiO₂ can provide enhanced corrosion protection capability for 211Z aluminium alloys compared with CeCC coating, it can not only statically block the contact between aluminium alloy substrate and corrosion medium, but also effectively provide dynamic response electrochemical corrosion protection in case of cracks or defects happening in the coating. The excellent corrosion protective ability of this coating can greatly expand the application field of 211Z high strength, toughness and heat resistant aluminium alloy. For example, promote its application in the vehicle lightweight field requiring anti-corrosion ability.
4. Conclusion

(1) The polarization curves and EIS results show that the CeCC-TiO$_2$ composite coatings with higher $E_g$ values display better anticorrosive performances, such as higher corrosion potential, greater coating resistance values and lower current density, as well as, the surface of coating will become more compact.

(2) The intergranular corrosion depth decreases with the increase of $E_g$ values of CeCC-TiO$_2$ composite coatings, which is 72 $\mu$m, 64 $\mu$m and 61 $\mu$m, corresponding to $E_g$ values of 3.07 eV, 3.38 eV and 3.51 eV,

Figure 5. Surface morphology variation of the scratches when the sample was soaked in 3.5 wt% NaCl solution at different time of (a) 0d, (b) 3d, (c) 10d, (d) 30d, and (e)–(f) 60d. The same scratched area marked by the red dashed line. (f) and (g) show the element composition of the Spectrum1 area in (a) and Spectrum2 area in (e), respectively.
respectively. All of them are lower than that of uncoated sample (89 μm). It is ascribed to that higher Eg value can bring more compact surface structure and improve the ability of blocking chloride ions across the coating.

(3) The self-healing ability of CeCC could be improved by adding TiO2 sol and the Eg value of the CeCC-TiO2 composite coating with the best self-healing performance is 3.38 eV. With the increase of the Eg values, the proportion of Ce3+ ions increase. Ce3+ ions have a dynamic protective effect so that it could move to the defect (scratch) to form Ce-Al-O layer and show excellent self-healing performances. However, when the proportion increases to a higher level, the effect is not as good as the inert barrier effect of Ce4+ ions.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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References

[1] Machkova M et al 2013 Effect of the anionic part of various Ce(III) salts on the corrosion inhibition efficiency of AA2024 aluminium alloy Corros. Sci. 69 396–405
[2] Azimi G et al 2015 Hydrophobicity of rare-earth oxide ceramics Nat. Mater. 12 315–20
[3] Zheludkevich M L et al 2007 On the application of electrochemical impedance spectroscopy to study the self-healing properties of protective coatings Electrochem. Commun. 9 2622–8
[4] Buchheit R G et al 1995 Chromate-free corrosion resistant conversion coatings for aluminum alloys Office of Scientific & Technical Information Technical Reports. (https://doi.org/10.2172/28379)
[5] Zhou S Y and Mao J 2019 Adjusting band gap of cerium conversion coating with TiO2 sol and its photocatalysis performance under ultraviolet irradiation Mater. Res. Express 6 086466
[6] Petrović S et al 2018 Optimization of a nanoparticle ball milling process parameters using the response surface method Adv. Powder Technol. 29 2129–39
[7] Tong T et al 2007 Preparation of Ce-TiO2 catalysts by controlled hydrolysis of titanium alkoxide based on esterification reaction and study on its photocatalytic activity J. Colloid. Interf. Sci. 315 382–8
[8] Aramaki K 2003 XPS and EPMA studies on self-healing mechanism of a protective film composed of hydrated cerium(III) oxide and sodium phosphate on zinc Corros. Sci. 45 199–210
[9] Divya S et al 2014 Intermediate Ce4+ defect level induced photoluminescence and third-order nonlinear optical effects in TiO2–CeO2 nanocomposites Appl. Phys. A-Mat. 114 315–21
[10] Wu X et al 2015 Improving the properties of 211Z Al alloy by enhanced electroless Ni-P-TiO2 nanocomposite coatings with TiO2 sol Surf. Coat. Technol. 270 170–4
[11] Yoganandan G, Pradeep Premkumar K and Balaraju J N 2015 Evaluation of corrosion resistance and self-healing behavior of zirconium–cerium conversion coating developed on AA2024 alloy Surf. Coat. Technol. 270 249–58
[12] Wang F and Mao J 2019 Nacre-like graphene oxide/waterborne styrene butadiene rubber composite and its reusable anti-corrosion behavior on Al-2024. Prog. Org. Coat. 132 191–200
[13] Castano C E, O’Keefe M J and Fahrenholz W G 2015 Cerium-based oxide coatings Corr. Opin. Solid State Mat. Sci. 19 69–76
[14] Aramaki K 2003 Self-healing protective films prepared on zinc electrodes by treatment in a cerium(III) nitrate solution and modification with sodium phosphate and calcium or magnesium nitrate Corros. Sci. 45 2361–76
[15] Heller D K, Fahrenholz W G and O’Keefe M J 2010 The effect of post-treatment time and temperature on cerium-based conversion coatings on Al2024-T3 Corros. Sci. 52 360–8
[16] Hinton B R W and Wilson L 1989 The corrosion inhibition of zinc with cerous chloride Corros. Sci. 29 967–75 977–85