

Preparation and characterization of Ce–silane–ZrO₂ composite coatings on 1060 aluminum

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Abstract: In order to improve the property of traditional Ce-based conversion coatings, Ce–silane–ZrO₂ composite coatings were successfully prepared on 1060 aluminum. The microstructure, chemical element composition and corrosion resistance of Ce-based conversion coatings and Ce–silane–ZrO₂ composite coatings were investigated by SEM, AFM, XPS and EIS analyses. Stacking structure of the composite coating can be observed. The inner layer of the composite coatings mainly consists of oxide and hydroxide of Ce(III), and the silane network is composed of the outer layer together with a small amount of Ce(IV) hydroxide. By adding silane and ZrO₂ nanoparticles into Ce-based conversion coatings, the porosity and the micro cracks of the coatings decrease apparently accompanying with the improvement of the corrosion resistance.

Key words: aluminum; conversion coatings; corrosion resistance; surface morphology; chemical composition

1 Introduction

Although Cr(VI)-based corrosion protection coatings have been applied to the protection of aluminum alloys against corrosion for over 50 years, it becomes obsolete gradually because of the carcinogenic nature and toxicity of Cr(VI). As an effective and environmentally friendly method to replace chromate conversion coatings, Ce-based conversion coatings (CeCCs) have been widely studied by many researchers since it was first proposed by HINTON et al [1–3]. Theoretically, Ce-based conversion coatings play the role of cathodic inhibitor [3,4] that precipitates at cathodic sites and inhibits the reaction of oxidizing species. As a kind of inorganic coatings, Ce-based conversion coatings have excellent ability of scratch resistance, durability and adhesion to the metallic substrate. What's more, the most special feature is its ability of self-heal, resulting from the interconversion of Ce³⁺ and Ce(OH)₂²⁺ ions [5]. However, the major problem of this method is the wide-range existence of cracks with the width more than 0.5 μm for CeCCs due to the interior stress resulting

from dewatering [6,7].

As another chromate alternatives, sol–gel derived organosilane films have attract much attention in recent years [8–10]. By immersing the substrate in hydrolyzed alcohol or water based silane solutions, a very dense self-assemble silane coating can be obtained, which can act as a physical barrier to delay the access of the aggressive species to metallic substrate [11]. However, there are still many challenges to restrict its further applications such as the low durability. Specially, silane cannot show corrosion inhibition properties, giving rise to the weak effect on improving the inhibition of the corrosion processes when the aggressive species reach the metallic substrate [12].

In this work, we immersed the Al matrix in the solution containing CeCl₃, BTESPT and ZrO₂ nanoparticles to prepare the composite coatings, which have the excellent performance of Ce-based conversion coatings and silane films. At the same time, ZrO₂ nanoparticles are added to get further improvement in aspects of thickness and density. And the role of nanoreservoirs for storage and controllable release of the inhibitor was also investigated for the nanostructured zirconia particles [13].

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2 Experimental

2.1 Solution preparation

The Ce-based conversion solution contained $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, NaF, benzotriazole and H_2O_2 . The solution pH was adjusted to 3 with HCl.

BTESPT silane solution was prepared by dissolving the bis-[3-(triethoxysilyl)propyl] tetrasulfide (BTESPT) (Urchem, China) (5%, volume fraction) in a mixture of anhydrous ethanol (90%, volume fraction) and deionized water (5%, volume fraction). The natural pH of the solution was 6.5. The mixture was continuously stirred for hydrolysis at room temperature for at least 2 d.

Nano-hybrid silane solution was prepared by adding ZrO_2 nanoparticles into BTESPT silane solution described above.

2.2 Coatings preparation

1060 Al substrates with dimensions of 25 mm×20 mm×0.8 mm were successively abraded with 600, 800, 1000, 1500 and 2000 grits emery paper, degreased with acetone and washed with deionized water. The substrates were ultrasonically alkaline cleaned with NaOH solution (20 g/L), Na_2CO_3 solution (50 g/L) respectively in an ultrasonic bath for 5 min each. The cleaned substrates were then rinsed in DI water.

1) Preparation of Ce-based conversion coatings

The substrates in the Ce-based conversion solution were immersed for 20 min, and then dried by hot air.

2) Preparation of Ce-silane- ZrO_2 composite coatings

The two sol solutions (Ce-based conversion solution and nano-hybrid silane solution) prepared from previous steps were combined together in 1:1 volume ratio. The substrates in the mixed solution were immersed for 20 min, and then dried by hot air.

2.3 Characterization

The surface morphologies and coating compositions were analyzed by scanning electron microscopy (SEM; JEDL JSM-6700F) and energy dispersive spectroscopy (EDS) was taken to analyze the elements existing on the surface. The morphology was also assessed by atomic force microscopy (AFM; Nanosurf easyScan) using a nanoscope digital instrument fitted with a nanoscopy III controller. The corrosion behavior of the specimens was monitored by electrochemical impedance spectroscopy (EIS) during immersion in 0.6 mol/L NaCl solution. Impedance measurements were recorded at open circuit potential (OCP) in a frequency range of 10 kHz to 10 mHz. XPS analysis was performed on a Thermo ESCALAB 250 X-ray photoelectron spectroscope using a monochromatic Al ($k_\alpha=1486.6$ eV). Detailed scans

were recorded for the Ce 3d and O 1s regions. The chemical interactions of the films were investigated by Fourier transform infra-red spectroscopy (FT-IR) using the thermo Nicolet instrument model NEXUS 670.

3 Results and discussion

3.1 Microstructure analyses

Figure 1 shows the SEM images of Ce-based conversion coatings and Ce-silane- ZrO_2 composite coatings. From Fig. 1(a), there is a large number of cracks with the width of 2 μm , which not only spread around the surface but also lurked in the inner layer (Fig. 1(b)). This phenomenon is common for coatings prepared by hydroxide gels in the previous literatures as the result of dehydration process of cerium conversion coatings [6,7,14,15]. By adding BTESPT and ZrO_2 nanoparticles, however, the more dense and homogeneous composite coatings without cracks can be obtained (Fig. 1(c)).

Figure 1(d) shows the high magnification SEM image of Ce-silane- ZrO_2 composite coatings, displaying a few of micro pores (diameter 10–50 nm). The deepness of micro-pores was so shallow that it was almost impossible to penetrate through the coatings. In addition, the stacking structure that can be seen from the SEM images reduces the probability that a single micro-pore or crack penetrates through the coatings, and thus this structure leads to very good barrier properties.

Figure 2 shows SEM cross-section image of Ce-silane- ZrO_2 composite coatings. As we can see from the cross-section micrograph, the thickness of composite coatings is 12–13 μm , which can further confirm that the micro-pores (diameter 10–50 nm) seen in Fig. 1(d) have almost no chance to extend themselves to the whole substrate surface.

Figure 3 shows EDX area analysis of Ce-silane- ZrO_2 composite coatings. The signals of Ce, Si, S and Zr indicated that $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, BTESPT, and ZrO_2 participated in the formation of the coating.

Figure 4 presents the atomic force micrographs (AFM) of Ce-based conversion coatings and Ce-silane- ZrO_2 composite coatings. As shown in Fig. 4(a), there are agglomerates of 1–3 μm in diameter on the surface of Ce-based conversion coatings. By adding BTESPT and ZrO_2 , the size of these agglomerates decreases to less than 1 μm (Fig. 4(b)), leading to the more smooth surface. This phenomena can be contributed to the slowing-down of the reaction of Ce^{3+} and OH^- by adding silane, decreasing the chances of the aggregation of deposit particles. And another reason may be that the ZrO_2 nanoparticles, as growing points, cause the uniformity of coatings due to their uniform distribution on the surface of the substrate.

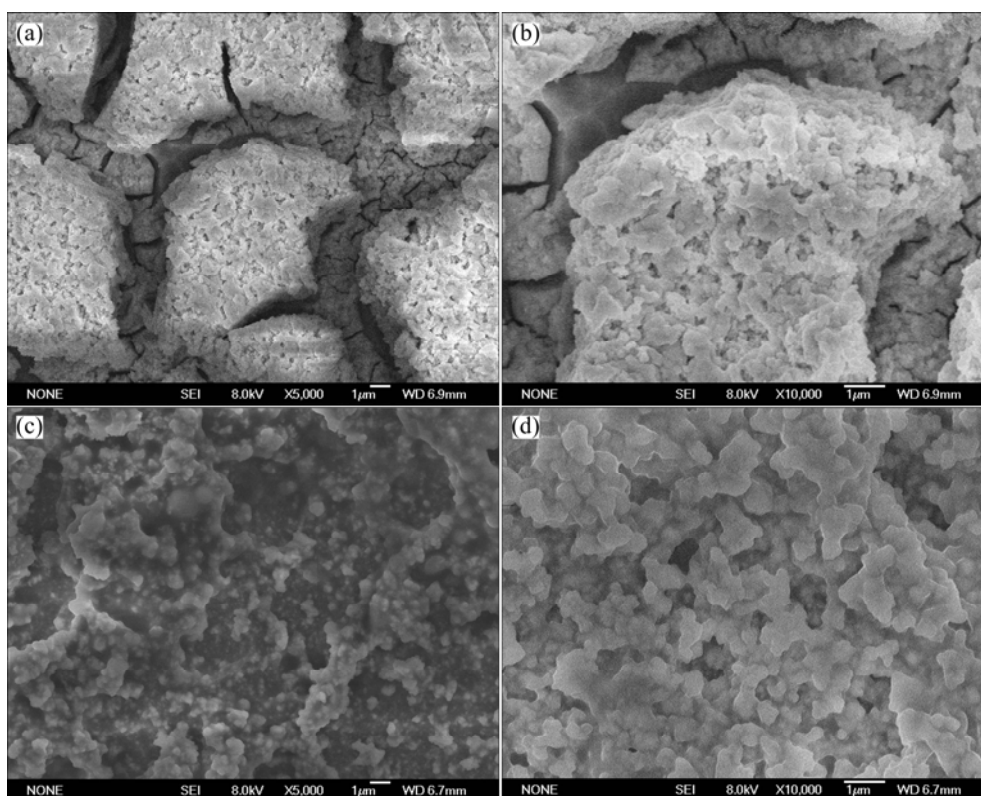


Fig. 1 SEM images of Ce-based conversion coatings (a,b) and Ce-silane-ZrO₂ composite coatings (c,d)

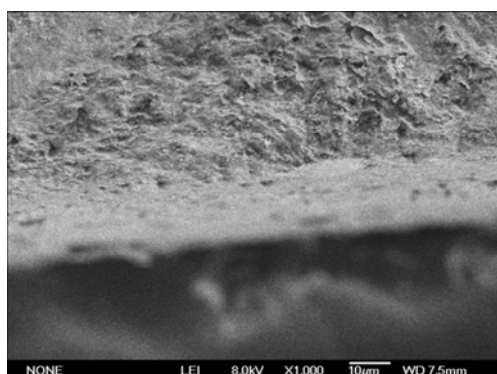


Fig. 2 SEM cross-section image of Ce-silane-ZrO₂ composite coatings

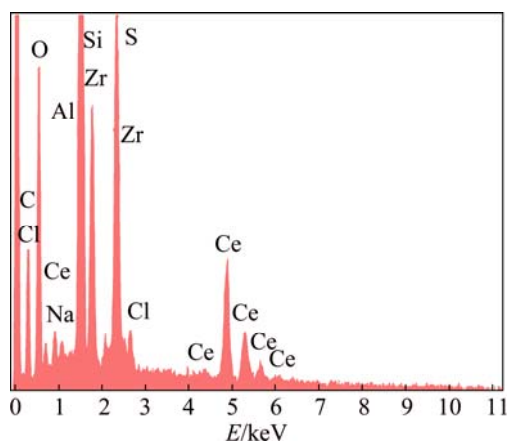


Fig. 3 EDX area analysis of Ce-silane-ZrO₂ composite coatings

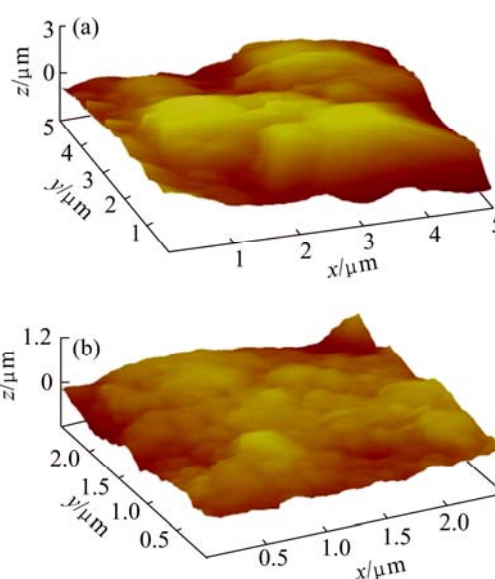


Fig. 4 Atomic force micrographs of Ce-based conversion coatings (a) and Ce-silane-ZrO₂ composite coatings (b)

3.2 Electrochemical measurements

In order to evaluate and compare the corrosion resistance of Ce-based conversion coatings and Ce-silane-ZrO₂ composite coatings, EIS studies were done for the 1060 Al samples treated in different conversion solutions. Figure 5 shows the EIS spectra (Nyquist and Bode plots) after 1 h immersion at 25 °C in 0.6 mol/L NaCl solution.

From Nyquist plots (Fig. 5(a)), it can be seen that

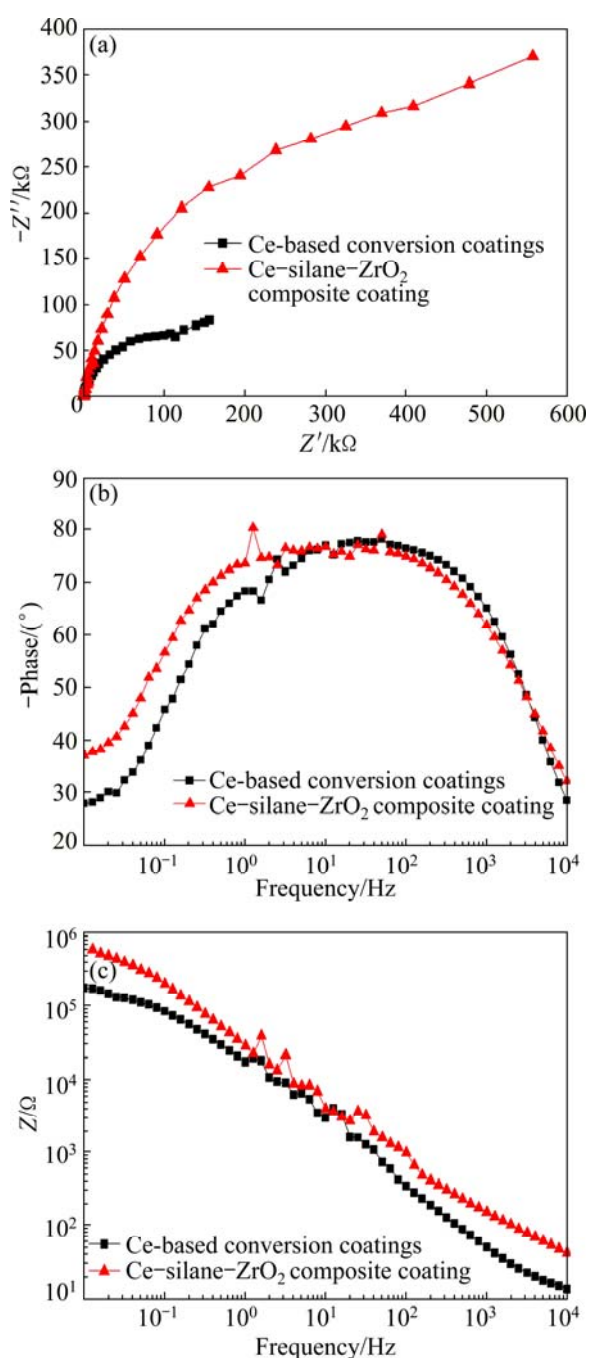


Fig. 5 Comparison of EIS spectra acquired from aluminum protected with different coatings: (a) Nyquist plots; (b) Bode phase plots; (c) Bode modulus plots

the curve diameter of Ce-silane-ZrO₂ composite coatings is larger than that of Ce-based conversion coatings, which shows the typical characteristic of capacitance. As seen from the Bode plots (Figs. 5(b) and (c)), the flattening region of the maximum in the Bode phase plots is very large for the composite coatings, indicating that the coating behaves closed to a capacitor. Additionally, in low frequency region and high frequency region, the value of Z for Ce-silane-ZrO₂ composite coatings was perceptibly increased (Fig. 5(c)).

This might result from the composite coatings with little cracks and pores, which acted as a physical barrier to penetration of electrolyte towards the metallic substrate and hindered the transmission of oxygen and electrons. Therefore, the corrosion current density was greatly reduced and the substrate was protected.

The EIS results were analyzed with ZSimpWin program using the equivalent circuit shown in Fig. 6, and the parameters obtained are listed in Table 1, where R_s represents the solution resistance. The electrochemical behavior of the coatings is represented by the capacitance C_p and pore resistance R_p . The corrosion process that occurs at the interface between the electrolyte and the substrate is represented by the double layer capacitance C_{dl} in parallel with the charge transfer resistance R_{ct} . The overall impedance, R_T , is the sum of R_p and R_{ct} .

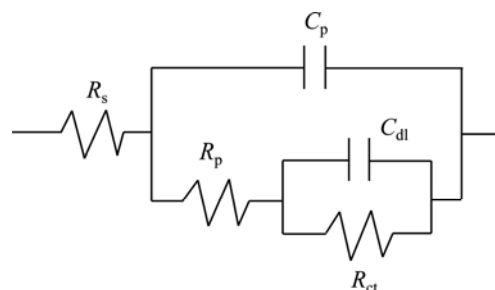


Fig. 6 Equivalent circuit model to fit impedance plots in Fig. 5

Table 1 Parameters obtained by fitting electrochemical data

Coating	$R_s/$ ($\Omega \cdot \text{cm}^2$)	$C_p/$ ($\mu\text{F} \cdot \text{cm}^2$)	$R_p/$ ($\text{k}\Omega \cdot \text{cm}^2$)	$C_{dl}/$ ($\mu\text{F} \cdot \text{cm}^2$)	$R_{ct}/$ ($\text{k}\Omega \cdot \text{cm}^2$)	$R_T/$ ($\text{k}\Omega \cdot \text{cm}^2$)
Ce	15.03	3.763	11.53	5.371	61.32	72.85
Ce-silane-Zr	15.27	1.919	95.15	3.751	818.6	913.8

It can be seen that the values of R_{ct} of BTESPT and ZrO₂ doped coatings are much higher than that of the coatings without BTESPT or ZrO₂, which can be explained that the zirconia particles play the role of nanoreservoirs for storage and controllable release of the inhibitor, and the continuously released oxides and hydroxides of Ce restrain the charge transfer. From the value of R_T , Ce-silane-ZrO₂ composite coatings show the better electrochemical performance.

3.3 Chemical composition analyses

Figure 7 shows the XPS survey spectra of the Ce-silane-ZrO₂ composite coatings with or without sputter. With 450 s sputter, the inner layer of the coating could be detected, showing the peaks of Si, O, Ce, S and C (partial C and O may be from contaminants during exposure to air). The element contents corresponding the survey spectra in Fig. 6 are shown in Table 2.

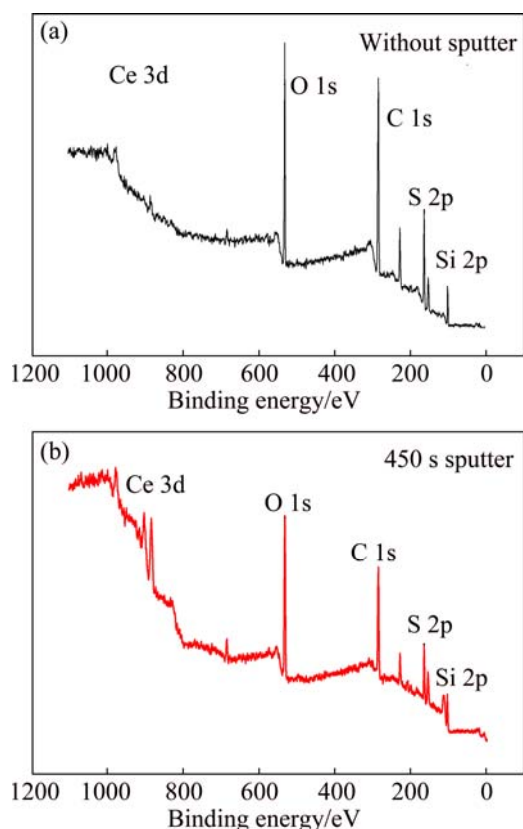


Fig. 7 XPS survey spectra of Ce-silane-ZrO₂ composite coatings

Table 2 Element content corresponding to survey spectra in Fig. 7

Layer	x(C)/ %	x(O)/ %	x(Ce)/ %	x(S)/ %	x(Si)/ %	x(Others)/ %
Outer	41.73	32.80	4.13	9.23	11.29	0.82
Inner	28.39	35.18	19.67	8.62	6.54	1.60

It is clear that the amount of Ce atoms in the inner layer has a greatly increase compared with the outer layer, while C and Si contents of the inner layer drop apparently. This can be explained as two reasons: one is the contaminants on coatings surface and the other is the low reaction activity of silane in the forming process of the films. At the early stage of film-forming, the main component was oxide and hydroxide of cerium, leading to the increase of Ce atoms in the inner layer. At the later stage, the substrate was almost covered, giving rise to the sharp decrease of the reactive speed of Ce³⁺ and OH⁻. The hydrolyzed silane connected with each other to form a network with the forces of hydrogen bonding Si—OH, forming the main component of the outer layer. Meanwhile, the micro cracks and pores in the inner layer were repaired.



The XPS high-resolution spectra of Ce 3d obtained from the Ce-silane-ZrO₂ composite coatings with or without sputter are shown in Fig. 8. The μ^{'''} peak, which arose exclusively from Ce⁴⁺ and was absent from the Ce 3d spectra of pure Ce³⁺ species, could be used as valence state analysis of Ce compounds and quantitative measure of the amount of Ce⁴⁺ [16]. It had been reported [17] that the percentage of Ce⁴⁺ account for the total Ce could be calculated by

$$n(\text{Ce}^{4+}) = \frac{n(\mu''')}{14} \times 100\% \quad (6)$$

where $n(\mu''')$ is percentage of μ^{'''} peak area with respect to the total Ce 3d area.

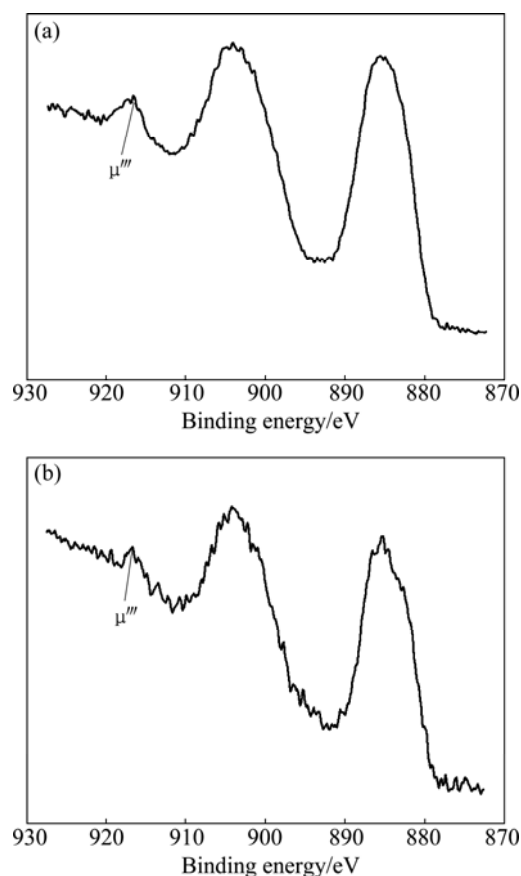
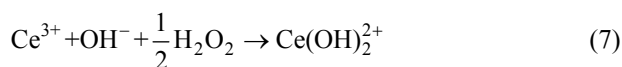


Fig. 8 Ce 3d spectra of Ce-silane-ZrO₂ composite coatings: (a) Without sputter; (b) 450 s sputter

Following the theory mentioned above, the percentage of Ce⁴⁺ in the inner layer can be calculated as only 19.1%, but 41.4% for the Ce⁴⁺ in the outer layer of composite coatings. This indicates that the inner layer is composed mainly of oxide and hydroxide of Ce(III), which could be due to the fact that H₂O₂ mostly

participated in the electrode reaction in the first step of film formation. And with the weakening of electrode reaction, a large proportion of H_2O_2 acted as oxidant as follows:



It was no surprise that there was more Ce(IV) detected in the outer layer.

The XPS high-resolution spectra of Ce 3d obtained from the Ce-silane- ZrO_2 composite coatings with or without sputter are shown in Fig. 9. Based on the assumption that the O 1s spectrum was attributed to the Ce—O group (529.5 eV), Si—OH group (531.6 eV), Ce—OH group (532 eV), and Si—O group (532.5 eV), O 1s spectra were fixed as shown in Fig. 9. According to area of the peaks, the value $[\text{O}_{\text{Ce-OH}}]/[\text{O}_{\text{Ce-O}}]$, $[\text{O}_{\text{Si-O}}]/[\text{O}_{\text{Si-OH}}]$ and $[\text{Si}]/[\text{Ce}]$ were obtained, as shown in Table 3.

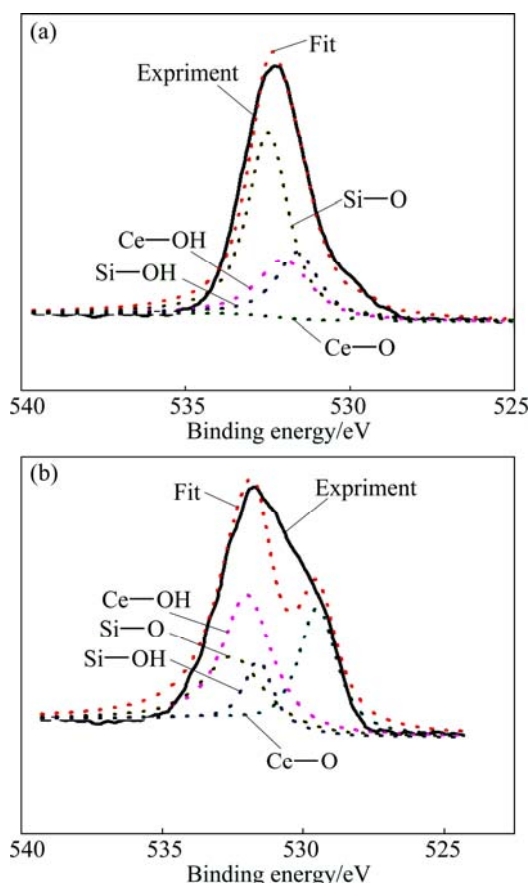


Fig. 9 O1s spectra of Ce-silane- ZrO_2 composite coatings: (a) Without sputter; (b) 450 s sputter

It can be seen that Ce is mainly present in the outer layer as its hydroxide, but in the inner layer the amounts of cerium oxide and hydroxide are not different largely. The value of $[\text{O}_{\text{Si-O}}]/[\text{O}_{\text{Si-OH}}]$ could reflect the degree of curing. As determined from Table 3, the crosslinking degree of BTESPT is over 70% and the value of $[\text{Si}]/[\text{Ce}]$ is basically consistent with that listed in Table 3.

Table 3 Values of $[\text{O}_{\text{Ce-OH}}]/[\text{O}_{\text{Ce-O}}]$, $[\text{O}_{\text{Si-O}}]/[\text{O}_{\text{Si-OH}}]$ and $[\text{Si}]/[\text{Ce}]$ obtained from Fig. 9

Layer	$[\text{O}_{\text{Ce-OH}}]/[\text{O}_{\text{Ce-O}}]$	$[\text{O}_{\text{Si-O}}]/[\text{O}_{\text{Si-OH}}]$	$[\text{Si}]/[\text{Ce}]$
Outer	20.2	2.58	3.16
Inner	1.29	2.21	0.52

Figure 10 shows the IR spectra of the Ce-silane- ZrO_2 composite coatings. The sharp peaks at 1037 cm^{-1} and 1107 cm^{-1} are characteristic of the silicon dioxide network (Si—O—Si). The high absorptive intensity suggests the high degree of curing. And the shoulder appearing on the side of this absorption (1249 cm^{-1}) indicates the presence of Si—O—R, which is provided by the non-hydrolysed BTESPT. Another shoulder appearing at 894 cm^{-1} can be ascribed to the presence of Si—OH, which results from the uncured silane. The vibration band at 2920 cm^{-1} is characteristic of alkyl groups (—CH, —CH₂ and —CH₃).

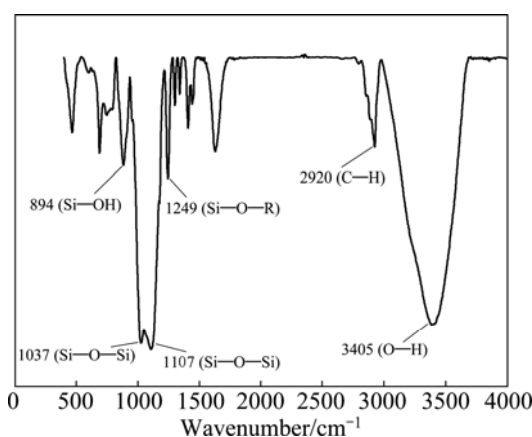


Fig. 10 IR spectra of Ce-silane- ZrO_2 composite coatings

4 Conclusions

A kind of Ce-based organic-inorganic hybrid coatings on 1060 aluminum was prepared and investigated. The addition of silane and ZrO_2 nanoparticles to Ce-based conversion coatings reduces the porosity and decreases the micro-cracks of the coating. As expected, the corrosion resistance of composite coatings is improved greatly, which was proved by the EIS analysis. The XPS results suggest that inner layer of the composite coating mainly consists of oxide and hydroxide of Ce(III), while silane network is composed of the outer layer together with a small amount of Ce(IV) hydroxide.

References

- [1] HINTON B R W, ARNOTT D R, RYAN N E. The inhibition of aluminum-alloy corrosion by cerous cations [J]. Metals Forum, 1984,

- 7(4): 211–217.
- [2] HINTON B R W. Corrosion inhibition with rare-earth-metal salts [J]. Journal of Alloys and Compounds, 1992, 180: 15–25.
- [3] HINTON B R W, ARNOTT D R, RYAN N E. Cerium conversion coatings for the corrosion protection of aluminium [J]. Materials Forum, 1986, 9(3): 162–173.
- [4] BETHENCOURT M. Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys: A review [J]. Corrosion Science, 1998, 40(11): 1803–1819.
- [5] HAYES S A. The phase stability of cerium species in aqueous systems—I. *E*-pH diagram for the Ce-HClO₄-H₂O system [J]. Journal of the Electrochemical Society C, 2002, 149(12): 623–630.
- [6] ZHITOMIRSKY I, PETRIC A. Electrochemical deposition of ceria and doped ceria films [J]. Ceramics International, 2001, 27(2): 149–155.
- [7] ZHITOMIRSKY I, PETRIC A. Electrolytic and electrophoretic deposition of CeO₂ films [J]. Materials Letters, 1999, 40(6): 263–268.
- [8] CUI Xue-jun, LIU Chun-hai, YANG Rui-song, LI Ming-tian, LIN Xiu-zhou, GONG Min. Phosphate film free of chromate, fluoride and nitrite on AZ31 magnesium alloy and its corrosion resistance [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(11): 2713–2718.
- [9] WANG M. Characterization of bis-triethoxysilylpropyl tetrasulfide layers on aluminum based on water-based silanization solution [J]. Thin Solid Films, 2012, 520(17): 5610–5615.
- [10] ZAND R Z, VERBEKEN K, ADRIAENS A. Corrosion resistance performance of cerium doped silica sol-gel coatings on 304L stainless steel [J]. Progress in Organic Coatings, 2012, 75(4): 463–473.
- [11] VANOOLIJ W. Corrosion protection properties of organofunctional silanes—An overview [J]. Tsinghua Science & Technology, 2005, 10(6): 639–664.
- [12] MONTEMOR M E, FEFEEIRA M G S. Cerium salt activated nanoparticles as fillers for silane films: Evaluation of the corrosion inhibition performance on galvanised steel substrates [J]. Electrochimica Acta, 2007, 52(24): 6976–6987.
- [13] ZHELUDKEVICH M L. Nanostructured sol-gel coatings doped with cerium nitrate as pre-treatments for AA2024-T3-Corrosion protection performance [J]. Electrochimica Acta, 2005, 51(2): 208–217.
- [14] HAMLAOUI Y. Cathodic electrodeposition of cerium-based oxides on carbon steel from concentrated cerium nitrate solutions part I. Electrochemical and analytical characterisation [J]. Materials Chemistry and Physics, 2009, 113(2–3): 650–657.
- [15] ARURAUULT L. Electrochemical preparation of adherent ceria coatings on ferritic stainless steel [J]. Thin Solid Films, 2004, 466(1–2): 75–80.
- [16] HUGHES A E, GORMAN J D, PATERSON P J K. The characterisation of Ce-Mo-based conversion coatings on Al-alloys [J]. Corrosion Science, 1996, 38(11): 1957–1976.
- [17] YU X, LI G. XPS study of cerium conversion coating on the anodized 2024 aluminum alloy [J]. Journal of Alloys and Compounds, 2004, 364(1–2): 193–198.

铝表面 Ce-硅烷-ZrO₂ 复合膜的制备及表征

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摘要: 为了改善传统稀土转化膜的性能, 运用浸泡法在铝表面制备 Ce-硅烷-ZrO₂ 复合膜。运用 SEM、AFM、XPS 和 EIS 等技术手段对复合膜层的微观形貌、化学组成和电化学性能进行研究, 并与 Ce 转化膜进行比较。Ce-硅烷-ZrO₂ 复合膜层表面呈堆砌结构, 膜内层主要由 Ce(III)的氧化物和氢氧化物构成, 而膜外层的主要成分是硅烷偶联聚合而成的大分子网状结构。与 Ce 转化膜相比, 加入硅烷和 ZrO₂ 纳米微粒后, 复合膜表面的微孔和裂纹都明显减少, 且耐蚀性能有了明显的改善。

关键词: 铝; 转化膜; 耐蚀性; 表面形貌; 化学组成

(Edited by Xiang-qun LI)