



A Dense Cr₂O₃/Al₂O₃ Composite Ceramic Coating Prepared by Electrodeposition and Sealing with Al₂O₃

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Abstract: A dense Cr_2O_3/Al_2O_3 composite coating was fabricated on 321L stainless steel by electrodepositing an Al_2O_3 layer on a Cr_2O_3 coating. The composition, structure, and properties of the obtained ceramic coating were investigated. The results showed that Al_2O_3 fully infiltrated the Cr_2O_3 coating and significantly improved the compactness of the ceramic coating by filling in the pores and cracks between the Cr_2O_3 grains. The composite ceramic coating was heat-treated at 750 °C and exhibited a high microhardness of 219.4 HV_{500g}, a bonding strength of 46.5 MPa, and excellent anti-corrosion and deuterium permeation suppression properties.

1. Introduction

Ceramic coatings on the surface of metal materials have wide application in power and refractory industries against chemical corrosion, oxidation, abrasive wear, and tritium permeation. Cr_2O_3 is regarded as an effective protective coating due to its thermal stability, chemical inertness, low permeability of hydrogen isotopes, and good adhesion to metal substrates. Up to now, Cr_2O_3 and its composite ceramic coatings have been made by magnetron sputtering [1,2], thermal spray [3–5], electrodeposition [6], atomic layer deposition, and evaporation [7]. Among these methods, electrodeposition is suitable for fabricating ceramic coatings on metal substrates because of its capability of complex geometries, possibility of coating different substrate materials, and easy operation. However, large porosity and cracking caused by thermal expansion and low heat-treatment temperatures may deteriorate coatings' properties and result in coatings with unsuitable properties. Therefore, it is necessary to modify the surface of Cr_2O_3 ceramic coatings by eliminating the surface porosity and reducing cracking. Wang et al. [8] covered a Cr_2O_3 coating with aluminum phosphate by dip-coating, which exhibited a good resistance to corrosion and improved tritium resistant performance. Shao et al. [9] prepared Cr_2O_3/Al_2O_3 composite coatings sealed by aluminum phosphate with a small fraction of Al₂O₃ nanoparticles. The sealants augmented the corrosion resistance properties of the coatings. Zhang et al. [10] fabricated plasma-sprayed Cr_2O_3/TiO_2 coatings deposited on mild steel and sealed by epoxy resin and silicone resin, which improved the corrosion resistance of the Cr_2O_3/TiO_2 coating significantly. However, the interface combination was poor, and cracks formed as a result of the heterogeneity of the coating and sealing materials.

 Al_2O_3 is also one of the most important oxide ceramics because of its high hardness, high chemical stability, and excellent wear and corrosion resistance. Some researches about the preparation of Al_2O_3 composites coating by electrodeposition have been reported [11–13]. Al_2O_3 can form an $(Al_{1-x}Cr_x)_2O_3$



infinite solid solution with Cr_2O_3 due to their similar crystal structure. By introducing an Al_2O_3 sealing layer, a good interface between Al_2O_3 and Cr_2O_3 can be expected.

In this work, Al_2O_3 was used as an effective sealing layer for Cr_2O_3 coatings. It was found that Al_2O_3 could fill up the pores and cracks of Cr_2O_3 , resulting in a uniform and dense composite coating. The microstructures and properties of the composite coating were investigated in detail.

2. Experimental

A Cr₂O₃ coating was firstly prepared by electroplating and heat treatment in accord with our previous report [8]. Briefly, a pure Pt plate was used the anode, and the 321L steel substrate, 29 mm in diameter and 0.5 mm in thickness, was used as the cathode. These two electrodes were placed parallel to each other and immerged into an electrolytic solution containing 220 g L⁻¹ chromium trioxide (CrO₃) and 2.2 g L⁻¹ sulfuric acid (H₂SO₄). The distance between the two electrodes was fixed to 40 mm. Electroplating was performed by setting the current density to 0.3 A cm⁻² for 80 min at 72 °C. Then, the as-deposited Cr sample was heat-treated at 700 °C for 4 h in air to transform Cr into Cr₂O₃.

An Al₂O₃ sealing layer was fabricated on the surface of the Cr₂O₃ coating by electrodeposition. The Cr₂O₃-coated specimen acted as the cathode, and the distance between the electrodes was 15 mm. The electrolytic deposition was carried out in 0.1 mol L⁻¹ Al(NO₃)₃·9H₂O solution at 10 A m⁻² for 10 min. Then, the sample was dried at 150 °C for 20 min. The above procedure was repeated twice. Finally, the specimens were heated at different temperatures in air for 1 h.

The phase composition and structure of the samples were identified by X-ray diffraction (XRD-6100, X-ray diffractometer with Cu K radiation, Shimadzu, Tokyo, Japan). The surface and cross section morphology were observed by a scanning electron microscope (SEM, Nova NanoSEM 450 microscope, FEI, Eindhoven, The Netherlands). The compositions of the coatings were examined by energy dispersive X-ray spectrometer (EDX). The chemical states were identified by X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600W, Kratos, Tokyo, Japan).

The Vickers hardness of the specimens were examined by a HV-1000 micro hardness tester (Wilson, Norwood, MA, USA) at 500 g for 15 s.

The CHI600b electrochemical analyzer (Chenhua, Shanghai, China) was used to test the electrochemical corrosion of the specimens. The test was conducted in 3.5 wt. % NaCl solution, and a saturated Ag/AgCl electrode was used as the reference electrode, platinum wire as the counter electrode, and the specimens coated with epoxy resin leaving an exposed surface area of 1 cm² as the working electrode. A potential scanning rate of 0.5 mV s^{-1} was adopted to gather all potentiodynamic measurements. The potential range was from -1 to 1 V. Corrosion current densities (I_{corr}) and corrosion potentials (E_{corr}) were evaluated according to the intersection of the linear anodic and cathodic branches of the polarization curves and were given by the ZView3.1 software.

The adhesion tensile test was performed to investigate the mechanical quality of the coatings, as illustrated schematically in Figure 1. The coated specimens were bonded to two fixtures by E7 glue, then placed into the oven and heated to 100 °C for 2 h. The fixtures were then connected with rods by the threaded holes. Tensile testing was performed by a Zwick/Roell 020 electronic universal testing machine (Shimadzu, Tokyo, Japan). The adhesive strength between the coating and the substrate was measured and evaluated from the tensile load at which the test specimen was broken [14].

The deuterium permeation properties were measured on a hydrogen isotope transmission suppression device at the Graduate School of Science, Shizuoka University. The apparatus and the procedure of permeation measurement are described in references [15,16]. The pressure of deuterium in the upstream part was kept at 10 kPa, and the pressure of deuterium permeating through the specimen into the downstream part was measured by a quadrupole mass analyzer. The measurements were carried out at 450–600 °C.



Figure 1. Sketch map of the adhesive strength tensile test.

3. Results and Discussion

Figure 2 shows the XRD patterns of the pre-sealed and post-sealed Cr_2O_3 coatings by heat treatment at various temperatures. All the diffraction peaks could be indexed to the standard patterns of the corundum structure Cr_2O_3 (JCPDS No. 38-1479) in all coatings. No new diffraction peaks appeared in the sealed coatings. With increasing temperatures, the diffraction peaks of Cr_2O_3 first decreased and then increased. The position of the peaks shifting to a higher angle was observed in the sealed samples at 750 °C. It is speculated that a thin Al_2O_3 layer covering the Cr_2O_3 coating led to the decrease of its diffraction peaks. The increasing and shifting peaks were due to Al ions entering Cr_2O_3 to form $(Cr_{1-x}Al_x)_2O_3$ solid solutions.



Figure 2. XRD patterns of the pre-sealed and post-sealed Cr_2O_3 coatings heat-treated at different temperatures.

Surface images of the unsealed and sealed coatings by heat treatment at different temperatures are presented in Figure 3. Figure 3a shows the unsealed coating, composed of Cr_2O_3 grains with pronounced grain boundaries. Its surface appeared rough with many pores. When this coating was sealed by an Al₂O₃ film and heat-treated at 650 °C (Figure 3b), the surface porosity decreased but more cracks were observed. The increase in heat-treatment temperature led to the cracks decreasing and the improvement of the surface state (Figure 3c). Almost all the porosity and cracks disappeared (Figure 3d) by increasing the temperature to 750 °C. This phenomenon can be explained as suggested by Olding et al. [17]. One main factor causing it was the residual H₂O and OH groups in the coating during the heat-treatment process. The Al₂O₃ precipitate contained H₂O and OH groups. The removal of these trapped groups at the heat-treatment temperatures led to the formation of micro-crackings in the sealed layer. Another factor leading to micro-cracking within the sealed layer was the thermal expansion mismatch between different materials. The slight difference between Cr_2O_3 (7 × 10⁻⁶/°C) and Al₂O₃ (7.85 × 10⁻⁶/°C) might be partially attributed to the cracks in the layer [18,19]. By increasing the temperature to 750 °C, cracking was avoided by grain rearrangement.

The porosity was calculated by image-pro software as shown in Figure 4. It was found that the porosity of the Cr_2O_3 (45.22%) coating was higher than that of all the composite coatings. When the heat-treatment temperature was 650 °C, the porosity of the coating surface was drastically reduced to 18.3%. The porosity decreased gradually with the increasing temperature. The porosity of the coating surface decreased to 1.98% when the heat-treatment temperature was 750 °C.



Figure 3. SEM images of the (**a**) unsealed and (**b**–**d**) sealed Cr_2O_3 coatings heat-treated at different temperatures: (**b**) 650 °C; (**c**) 700 °C; (**d**) 750 °C.



Figure 4. Porosity of the Cr_2O_3 coating and the sealed Cr_2O_3 coatings heat-treated at different temperatures.

Figure 5 presents the cross-sectional back-scattered electron images of the sealed coating before and after it was heat-treated at 750 °C. The as-deposited coating consisted of two distinct layers with the sealed Al_2O_3 as the outer layer of 0.38 µm, and the Cr_2O_3 as the inner layer of 9.00 µm. However, when the sealed coating was heat-treated, the Al_2O_3 outer layer was difficult to identify. It is interesting to note that the high substrate roughness was attenuated by the sealed layer. In addition, no cracks and holes were observed in the coatings, indicating a dense and homogeneous morphology.

To give more insights into the effect of the sealing layer, the compositions of the cross section of the sealed coating before and after heat treatment at 750 °C was analyzed by EDS. The corresponding element maps are shown in Figure 6. It is clearly observed from Figure 6a that Al element was uniformly distributed in the sealed layer, suggesting that a uniform Al_2O_3 layer formed; the EDS elemental maps of the heat-treated sealed coating (Figure 6b) show that Al element was uniformly

distributed in the whole Cr_2O_3 coating, suggesting that a uniform Al_2O_3/Cr_2O_3 composite ceramic coating was formed.







Figure 6. Cross-sectional SEM image and EDS elemental maps of the sealed coating: (**a**) before heat treatment; (**b**) after heat treatment at 750 °C.

In order to identify the chemical states of Al, Cr, and O, XPS analysis was performed. Figure 7a displays that the binding energies of Cr $2p_{1/2}$ and Cr $2p_{3/2}$ were located at 586.6 and 577.1 eV, respectively, which correspond to Cr^{3+} of Cr_2O_3 in accordance with the values previously reported in the literature [20]. The XPS spectra of Al 2p (Figure 7b) revealed that there was a peak at 75.4 eV, which corresponded to the binding energy of Al₂O₃. Furthermore, a second peak at a low binding energy (74.4 eV) developed considerably, indicating the breakdown of Al–O bonds and the formation of a complex oxide Cr–O–Al [21]. Figure 7c shows the O 1s XPS spectrum which could be deconvoluted into two peaks at 530.7 and 532.0 eV, respectively. According to the literature [22,23], O 1s binding energy (BE) values for Cr₂O₃ change from 530.0 to 530.8 eV, while those for Al₂O₃ appear to be around 531.6 eV. Therefore, the O 1s peak positions of 530.7 eV was attributed to Cr₂O₃, while that located at 532.0 eV was attributed to Al₂O₃.

The above results further illustrate that after heat treatment, Al_2O_3 could significantly improve the compactness of the Cr_2O_3 coating by filling in the pores and cracks between the Cr_2O_3 grains. Furthermore, Al_2O_3 could fully infiltrate the coating, and elemental Al diffused into the Cr_2O_3 to form a solid solution.

The influence of the temperature on the hardness of the composite coatings is plotted in Figure 8 together with the data for the Cr_2O_3 coating. Because of the surface pores, Vickers hardness of the Cr_2O_3 coating was low at only 189 HV_{500g}. After fabricating the sealing layer, the hardness of the coating was improved because the surface pores were sealed. Meanwhile, it can be seen that Vickers hardness increased with the rising temperature, which was to the grain size effect and solid solution strengthening.



Figure 7. XPS spectra for (**a**) Cr 2p, (**b**) Al 2p, and (**c**) O 1s recorded on the sealed coating heat-treated at 750 °C.



Figure 8. Vickers hardness of Cr_2O_3 and Al_2O_3/Cr_2O_3 composite coatings heat-treated at different temperatures.

To confirm the sealing performance of the Al_2O_3 layer, the samples were characterized by electrochemical corrosion tests. Figure 9 shows the potentiodynamic polarization curves of Cr_2O_3 and Al_2O_3/Cr_2O_3 composite coatings at different temperatures. In the polarization curves, positive corrosion potential and negative corrosion current density represent lower corrosion rate and good anti-corrosion behavior. The electrochemical parameters calculated from the polarization curves are listed in Table 1. From Figure 9 and Table 1, it can be seen that the corrosion potential of the composite coating at 650 °C shifted about 31.0 mV (vs Ag/AgCl) to a positive direction, while the corrosion current density decreased to 1.32×10^{-9} A cm⁻², lower than that of the Cr_2O_3 sample. With the increase of temperature, the corrosion potential persistently increased, and the corrosion current density decreased continually. The composite coating at 750 °C exhibited the best corrosion resistance with a current density of 6.64×10^{-10} A cm⁻² and a corrosion potential of 224.0 mV.



Figure 9. Potentiodynamic polarization curve of Cr_2O_3 and Al_2O_3/Cr_2O_3 composite coatings heat-treated at different temperatures.

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	Sample	E _{corr} (vs. Ag/AgCl)/mV	$I_{\rm corr}$ (A cm ⁻²)
	Cr ₂ O ₃	92.0	$5.78 imes10^{-9}$
	Cr ₂ O ₃ /Al ₂ O ₃ coating at 650 °C	123.0	$4.46 imes 10^{-9}$
	Cr_2O_3/Al_2O_3 coating at 650 °C	176.0	$3.54 imes10^{-9}$
	Cr_2O_3/Al_2O_3 coating at 650 °C	224.0	$6.64 imes10^{-10}$

Table 1. Summary of the electrochemical parameters obtained from the potentiodynamic polarization curves for the unsealed and sealed coatings heat-treated at different temperatures.

The bonding strength between the coating and the metal substrate was measured through a pull-off method with a strain rate of 0.6 mm min⁻¹. The final bonding strength value was determined as the average strength measured for three samples that had been tested in the same conditions. The results are shown in Figure 10. It was found that the bonding strength of all the composite coatings was higher than that of the Cr_2O_3 coating. The bonding strength increased gradually with the temperature. When the temperature was 750 °C, the bonding strengths was up to 46.5 MPa. This is because at high temperatures, Al_2O_3 is capable of filling in the pores and cracks of the Cr_2O_3 coating. Additionally, elemental Al diffuses into Cr_2O_3 and favors the solid phase sintering reaction, improving the bonding strength of the coating. At the same time, chemical potential concentration differences of elements exist between the coating and the metal substrate. Under the driving actions of such concentration differences, elements such as Al and Cr diffuse and migrate into the substrate to reach the metal lurgical bonding state, which further improves the bonding between the ceramic phase and the metal phase.



Figure 10. Bond strength curves of the Cr_2O_3 and Al_2O_3/Cr_2O_3 composite coatings heat-treated at different temperatures.

To further evaluate the sealing properties of the composite coating, the deuterium permeability of the coated samples as a function of temperature was investigated, as shown in Figure 11. The permeation data of 321L stainless steel measured in this work was used for comparison. The permeability reduction factor (*PRF*) was defined as:

$$PRF = P_0/P \tag{1}$$

where P_0 and P are the deuterium permeability of the 321L stainless steel without and with coating, respectively. The *PRF* values of the coated samples were evaluated to be 1800, 717, 366, and 302 at 450, 500, 550, 600 °C, respectively, indicating that the composite coatings were all effective in reducing the hydrogen permeability. These values are higher than those for Cr_2O_3 films obtained with other methods [24].



Figure 11. Deuterium permeabilities of the Cr₂O₃/Al₂O₃ coated sample.

Figure 12 shows the dependence of the permeation flux on the driving pressure in the coated samples when evaluating the deuterium permeation regime of the composite coating. The pressure exponent *n* can be obtained by the linear relation of the ln *P*–ln *J*. The exponent *n* represents different permeation regimes: diffusion-limited and surface-limited when n = 0.5 and 1, respectively. In this work, the exponent *n* showed a value of 0.82–0.70 at 450–550 °C, which indicated that deuterium passed through the samples mainly in the surface-limited permeation mode. At 600 °C, however, the pressure exponent decreased to 0.53, indicating the rate-limiting process had changed from surface-limited to diffusion-limited in the coating.



Figure 12. Deuterium permeation flux through the composite coated sample as a function of the driving pressure at different temperatures.

4. Conclusions

A dense Cr_2O_3/Al_2O_3 composite coating was fabricated by electrodepositing an Al_2O_3 layer on a Cr_2O_3 coating. Heat-treatment of the sealed coating allowed the Al_2O_3 layer to fully infiltrate the Cr_2O_3 coating forming an Al_2O_3/Cr_2O_3 composite coating and significantly improving the compactness of the ceramic coating by filling in the pores and cracks between the Cr_2O_3 grains when the temperature reached 750 °C. The composite ceramic coating exhibited the high microhardness of 219.4 HV_{500g}, bonding strength of 46.5 MPa, and better anti-corrosion properties than the Cr_2O_3 coated-sample. In addition, its deuterium permeation flux was lower than that of the Cr_2O_3 coated-sample.

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