

Article

Corrosion and Wear Properties of Cr Coating and ZrO₂/Cr Bilayer Coating on Zr-4 Alloy

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Abstract: In this study, duplex surface treatments were used to prepare a ZrO₂/Cr bilayer coating on zirconium alloy cladding for enhancing the wear and corrosion behaviors. The surface and cross-section morphology of coated Zr-4 alloy was characterized; the results show that the Cr- and ZrO₂/Cr-coated samples had similar morphology, and more obvious surface undulates could be observed on the ZrO₂/Cr coating than the pure Cr coating owing to the rough surface of the plasma electrolytic oxidation coating. Wear and electrochemical behavior in 1200 mg/L H₃BO₃ and 2.2 mg/L LiOH solutions of original and coated Zr-4 alloy were investigated. The electrochemical corrosion test indicated the coated Zr-4 alloy exhibited better corrosion resistance behavior than the original Zr-4 alloy. The potentiodynamic polarization curves and corrosion morphology suggest the pitting corrosion occurred on the surface of the original and coated Zr-4 alloy. The ZrO₂/Cr-coated Zr-4 alloy had better corrosion resistance due to the dual protection of the PEO layer and Cr coating. The wear behavior of the original and coated Zr-4 alloy was also investigated under a constant load of 5 N. The results reveal that the coated Zr-4 alloy had better wear resistance, and the PEO layer was found to significantly enhance the wear resistance of the Zr-4 alloy.

Keywords: ZrO₂/Cr coating; Zr-4 alloy; corrosion; wear; thin films



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1. Introduction

The general public usually regards commercial nuclear power as a risk or unstable process, and it is erroneously associated with radiation, nuclear weapons and nuclear safety incidents. In fact, nuclear reactors generate electricity by using the heat energy released when certain elemental atoms are split apart, according to Ref. [1], which play an important role in energy conservation and emission reduction. Meanwhile, the safety of nuclear reactors in the process of nuclear energy applications is becoming more of a concern.

Nuclear fuel cladding has been regarded as the first safety barrier in nuclear reactors. After the Fukushima Daiichi nuclear accident, accident tolerant fuel (ATF)-coated Zr alloy has attracted worldwide attention due to its higher safety under accident conditions compared with the current Zr alloy cladding [2]. The potential ATF candidate coating mainly includes the MAX phase, FeCrAl, Cr, etc. Among them, Cr coating is considered the most promising material owing to its corrosion resistance, optimal high-temperature oxidation resistance and low thermal expansion coefficient difference with the Zr alloy matrix [3–7].

However, there are still some problems restricting the practical application of Cr coating. During the rise to a high temperature, the formation of brittle intermetallic compounds between the Cr coating and Zr alloy matrix can lead to cracks and spalling of the coating and weaken the protective effect on Zr cladding [8,9]. Furthermore, the eutectic reaction between Zr alloy and Cr coating (1330 °C and above) could lead to fast Cr-Zr interdiffusion, which causes the mechanical degradation and early failure of the Cr coating [10,11]. On the other hand, there is a large potential difference across the Zr alloy and Cr coating ($\Delta E = 0.809$ V). When microcracks appear in the Cr layer, the bimetallic

effect can accelerate the oxidation of the Zr alloy in the diffusion interface, and galvanic corrosion easily occurs at the Cr/Zr interface [12,13].

To solve this problem, the current research demonstrates that the introduction of an intermediate transition layer between zirconium alloy and Cr coating can effectively prevent the generation of brittle intermediate compounds under high-temperature conditions, and improve the high-temperature corrosion resistance of zirconium alloy [2,14]. Plasma electrolysis oxidation (PEO) can in situ generate a ZrO_2 layer on the surface of zirconium alloy, which has attracted properties such as high-bonding strength and good compatibility with zirconium alloy by adjusting parameters. Moreover, studies show a strong binding force between the ZrO_2 transition layer and Cr coating, which also maintains integrity after a long time at high temperatures. Furthermore, the thermal expansion coefficient of ZrO_2 matches Cr coating better than the zirconium substrate at about 1000 °C, as shown in Table 1 [15–17].

Table 1. Thermal expansion coefficients of Zr, ZrO_2 and Cr.

Property \ Material	Zr [15] 25–870 °C	ZrO_2 [16] 25–1040 °C	Cr [17] 25–1020 °C
thermal expansion coefficient ($\times 10^{-6}/\text{K}$)	5.5 (a axis)	10.3 (a axis)	16.6

Note: a axis indicates the expansion coefficients along the a axis in hcp lattice of Zr and expansion coefficients along the a axis of monoclinic ZrO_2 .

In the study of Wang et al. (2018) [18], $\text{ZrO}_2/\text{FeCrAl}$ double-layer coating was prepared on the surface of Zr-4 alloy by using plasma electrolytic oxidation (PEO) combined with magnetron sputtering. After steam oxidation at 1000 °C, it was found that the oxidation rate of $\text{ZrO}_2/\text{FeCrAl}$ -coated Zr-4 alloys was about 20 times lower than that of uncoated and FeCrAl-coated Zr-4 alloys. As for the study of Wang et al. (2021) [2,19], ZrO_2/Cr double-layer coating was prepared on Zr-1Nb alloy by plasma electrolytic oxidation combined with cathodic vacuum arc deposition. Their research results show that after high-temperature steam oxidation at 900–1100 °C, the oxidation weight gain of the Zr alloy with ZrO_2/Cr coating was much lower than that of the Zr alloy with Cr coating.

However, the current research on zirconium alloy with ZrO_2/Cr coating is predominantly focused on its high-temperature oxidation resistance and fails to consider the continuous scouring of high-temperature, high-pressure cooling water on cladding during service, leading to wear of cladding, simultaneous suffering from corrosion through chemicals and wear products in primary water, which will further aggravate the cladding abrasion, and even lead to perforation, resulting in leakage of fission products, affecting the safe operation and service life of the entire nuclear fuel assembly [20].

Considering the above, in this study, the ZrO_2/Cr bilayer coating was prepared on a Zr-4 alloy through duplex surface treatments—plasma electrolytic oxidation (PEO) followed by multi-arc ion plating. The influence of the ZrO_2 interlayer on the wear and corrosion properties was investigated. Moreover, the wear and corrosion resistance of the ZrO_2/Cr bilayer coating was evaluated in comparison with the original and Cr-coated Zr-4 alloy. It is hoped that this study can provide some suggestions on the development and application of ATF coating.

2. Materials and Methods

2.1. Materials and Preparation

Commercial Zr-4 alloy (Xi'an Western Energy Material Technologies Co., Ltd., Xi'an, China) with a size of 20 mm $\times$ 20 mm $\times$ 1.5 mm was used as a substrate. The chemical composition(wt.%) of the Zr-4 alloy was Sn 1.2%~1.7%, Fe 0.18%~0.24%, Cr 0.07%~0.13%, C ~0.027%, O ~0.16% and Zr balance. Prior to the coating process, the Zr-4 alloy was polished with SiC sandpaper up to a 2000 grit size followed by polishing the mirror surface with diamond paste, and then ultrasonic cleaning was carried out in acetone, anhydrous ethanol and deionized water for 15 min.

The ZrO_2 PEO coating on the Zr-4 alloy was fabricated by a dual-pulse voltage power (FLB-MAO200A, Xi'an Precision Technology Co., Ltd., Xi'an, China). The applied positive and negative voltages were +500 and -60 V, respectively. A pulse frequency of 150 Hz with a duty cycle of 6% was applied. The electrolyte contained 15 g/L NaAlO_2 , 1 g/L KOH, 4 g/L Na_2WO_4 and 30 mL/L glycerol. The Zr-4 alloy was oxidized at a solution temperature below 30°C for 20 min. Finally, Cr coating on the Zr-4- and ZrO_2 -coated Zr-4 samples was deposited by using multi-arc ion plating (MA1210-2450, Xi'an, China) in an atmosphere of Ar with a flow rate of 1800 sccm. The bias voltage was -120 V, and the working pressure was kept at 1.5 Pa during the deposition. Cr target with 99.9% purity was used to generate plasma at the 120 A arc current with a duty ratio of 50%, and the chamber temperature was kept constant at 300°C . The schematic diagram of the sample preparation process is shown in Figure 1.

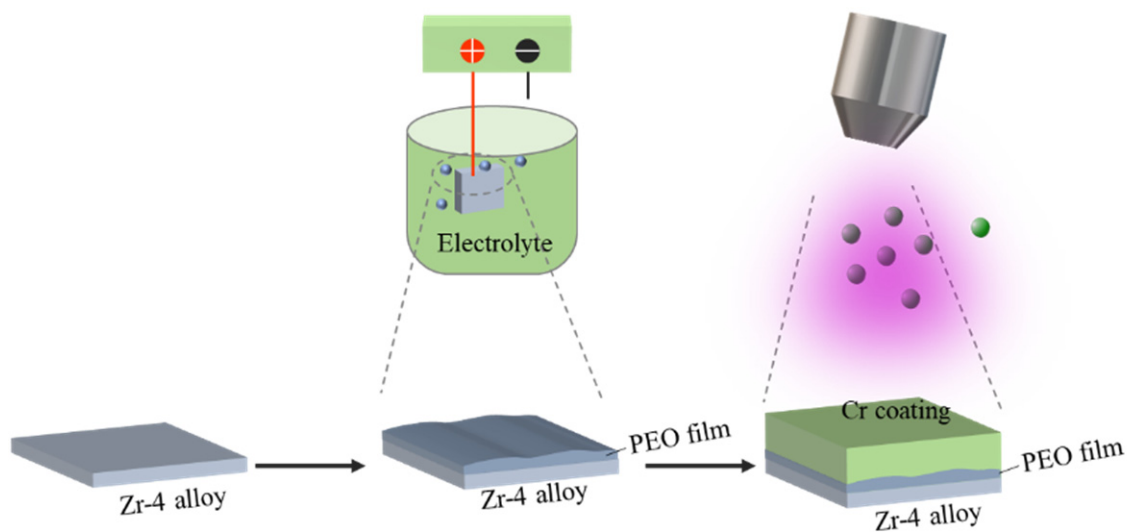


Figure 1. The schematic diagram of sample preparation.

2.2. Electrochemical Measurements and Wear Property Test

An electrochemical corrosion test was conducted by using a CS350M electrochemical workstation (Wuhan CorrTest Instruments Co., Ltd, Wuhan, China). The original Zr-4 alloy and coated Zr-4 alloy were used as the working electrode, a saturated calomel electrode (SCE) was used as a reference electrode, and a Pt plate was used as a counter electrode. The solution used in the electrochemical test was 1200 mg/L H_3BO_3 and 2.2 mg/L LiOH [21], which simulated the solution in a reactor. The potential dynamic polarization (PDP) curve test and electrochemical impedance spectroscopy (EIS) curves were tested after 90 min of exposure at open-circuit potential (OCP). PDP tests were performed with a scanning rate of 1 mV/s in the potential range of -1.5 to 1.5 V, and the EIS tests were carried out in the frequency range of 10^2 – 10^5 Hz.

Wear property tests were carried out on the original and coated Zr-4 alloy using a multifunctional friction and wear tester (MFT4000, Lanzhou Huahui Instrument Technology Co., Ltd., Lanzhou, China) under dry sliding conditions. The tests were performed using 5 N of loading against a ZrO_2 ball (6 mm diameter), a stroke length of 5 mm, and a sliding speed of 50 mm/min with a wear time of 10 min. After the wear test, the wear surface of wear track areas was measured, and the wear volume was calculated. The adhesion strength of substrate–coating was tested by using a multifunctional friction and wear tester (MFT4000). The scratch length was selected as 5 mm, and the progressive load ranged from 1 to 50 N with a speed of 25 N/min.

2.3. Characterizations

The surface morphology and cross-sectional microstructure of the Cr-coated and ZrO_2/Cr -coated Zr-4 alloy were characterized by scanning electron microscopy (SEM, ZEISS Gemini 300, Oberkochen, Germany). Chemical composition and line scanning of the cross-section of the Cr-coated and ZrO_2/Cr -coated Zr-4 alloy were measured by using energy-dispersive spectroscopy equipment (EDS, OXFORD Xplore, Oxford, UK).

3. Results and Discussion

The results and analysis are presented as following. Surface and cross-section morphology of Cr and ZrO_2/Cr coating on the Zr-4 alloy was observed first, corrosion and wear behaviors of Cr and ZrO_2/Cr coating were then evaluated and compared.

3.1. Morphology

Figure 2a shows the surface morphology of the ZrO_2 layer deposited by PEO; it could be observed that there were many micropores, cracks and volcano-like structures on the coating surface, which is a typical morphology of PEO coating, and a similar phenomenon was reported in other research [21]. The generated micropores could be attributed to the discharge breakdown on the surface of samples. In addition, in the process of plasma electrolytic oxidation, the expansion coefficients and directions of each oxide phase are different, and the melting and solidification of the sample surface is usually accompanied by a certain volume change, which results in the generation of thermal stress and cracks. Since the micropore is the center of stress concentration, the crack usually passes through the micropores [21–23]. Figure 2b,c depict the surface morphology of the Cr layer and ZrO_2/Cr bilayer coating, showing similar morphology and indicating that a smooth and dense Cr layer was deposited on the surface of the original and ZrO_2 -coated Zr-4 alloy, while some small particles were observed on the surface. However, no obvious defects such as micropores and cracks were observed. In addition, more obvious surface undulates could be observed on the ZrO_2/Cr coating than on the pure Cr coating, which may be ascribed to the rough surface of the PEO coating.

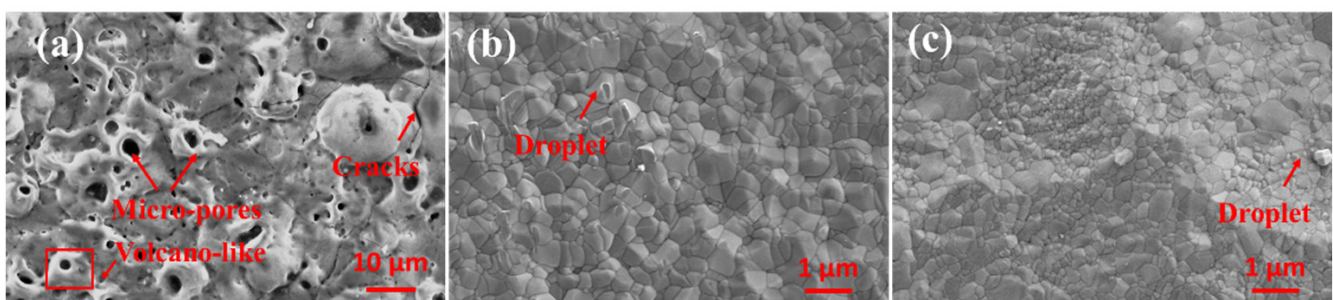


Figure 2. Surface morphology of the (a) ZrO_2 layer, (b) Cr outer layer and (c) ZrO_2/Cr bilayer coating.

Figure 3 illustrates the cross-section morphology and line scanning of Cr and ZrO_2/Cr coating on the Zr-4 alloy. Figure 3a shows that the Cr coating was uniform and dense with a thickness of about $2.6\ \mu\text{m}$. Figure 3b suggests that the PEO layer of ZrO_2/Cr coating consisted of a dense inner layer with a thickness of about $3.7\text{--}5\ \mu\text{m}$ and a porous outer layer with a thickness of about $6.7\text{--}9\ \mu\text{m}$. Microcracks induced by volume shrinkage can be observed in the inner layer, and micropores with a diameter of $0.3\text{--}0.45\ \mu\text{m}$ appeared in the outer layer. The Cr coating deposited on the PEO layer was dense and partly filled with the defects and micropores in the PEO coating during deposition.

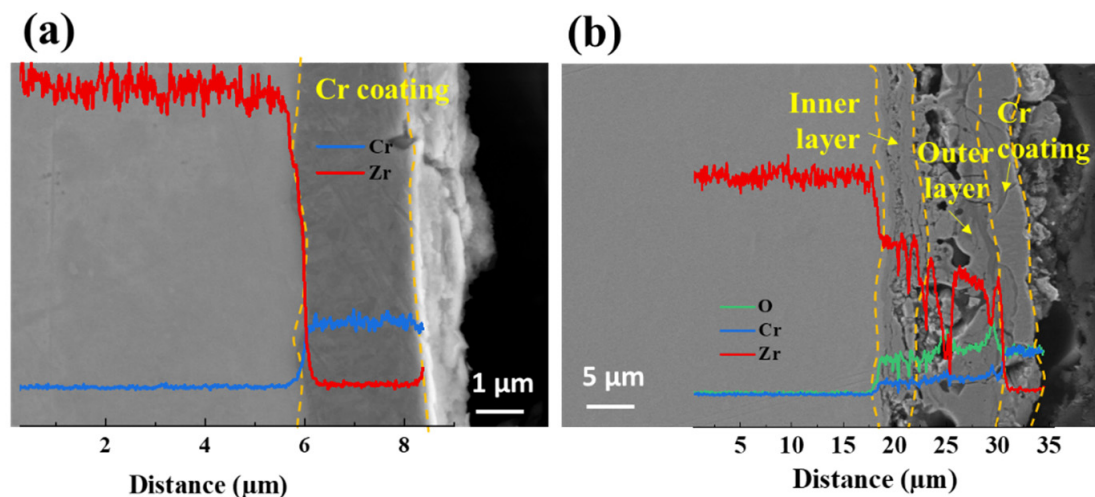


Figure 3. Cross-section morphology of (a) Cr and (b) ZrO_2/Cr coating on Zr-4 alloy.

3.2. Electrochemical Corrosion Measurement

Figure 4 shows the potentiodynamic polarization curves for the original, Cr-coated and ZrO_2/Cr -coated Zr-4 alloys. Corrosion current density (i_{corr}) and corrosion potential (E_{corr}) of the original, Cr-coated and ZrO_2/Cr -coated Zr-4 alloys were obtained using the Tafel extrapolation method, and the results are exposed in Table 2. The E_{corr} of the coated Zr-4 alloy (-0.847 V for Cr-coated and -0.702 V for ZrO_2/Cr -coated alloys) shifted to a more positive region compared with that of original the Zr-4 alloy (-1.216 V), which can be attributed to the presence of dense surface coating. The i_{corr} of the coated Zr-4 alloy (6.42×10^{-6} A/cm² for the Cr-coated Zr-4 alloy and 1.86×10^{-6} A/cm² for the ZrO_2/Cr -coated Zr-4 alloy) was lower than that of the original Zr-4 alloy (1.02×10^{-5} A/cm²), which reveals the coated Zr-4 alloy exhibited better corrosion resistance behaviors than the original Zr-4 alloy. The deterioration of corrosion performance is mainly ascribed to the dense surface, which prevented corrosion during electrochemical corrosion. In addition, the ZrO_2/Cr -coated Zr-4 alloy had better corrosion resistance due to the dual protection of the PEO dense inner layer and outer dense Cr coating. Moreover, the original and coated Zr-4 alloys were passivated at the anode, and a sharp rise appeared in the anodic region, which suggests the pitting corrosion occurred on the surface of the sample [24].

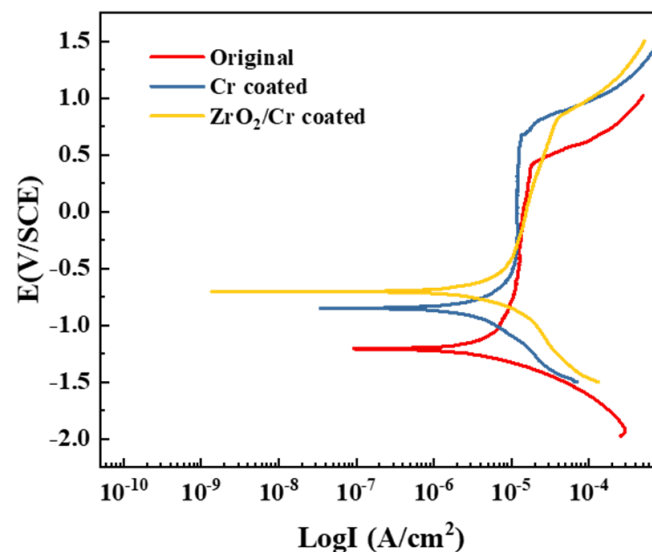


Figure 4. Potentiodynamic polarization curves for the original, Cr-coated and ZrO_2/Cr -coated Zr-4 alloys.

Table 2. Corrosion parameters of the original, Cr-coated and ZrO₂/Cr-coated Zr-4 alloy obtained from polarization curves.

Sample	E _{corr} (V/SCE)	i _{corr} (A/cm ²)
Original Zr-4 alloy	−1.216	1.02×10^{-5}
Cr-coated Zr-4 alloy	−0.847	6.42×10^{-6}
ZrO ₂ /Cr-coated Zr-4 alloy	−0.702	1.86×10^{-6}

The corrosion morphology of the original, Cr-coated and ZrO₂/Cr-coated Zr-4 alloys is shown in Figure 5. It can be clearly observed that pitting corrosion was present on the surface of all samples, which is consistent with the results in Figure 4. For the original Zr-4 alloy (Figure 5a), it can be seen that localized corrosion occurred except for the pitting corrosion. In addition, such corrosion of coated samples is hard to observe owing to the protection of the dense coating.

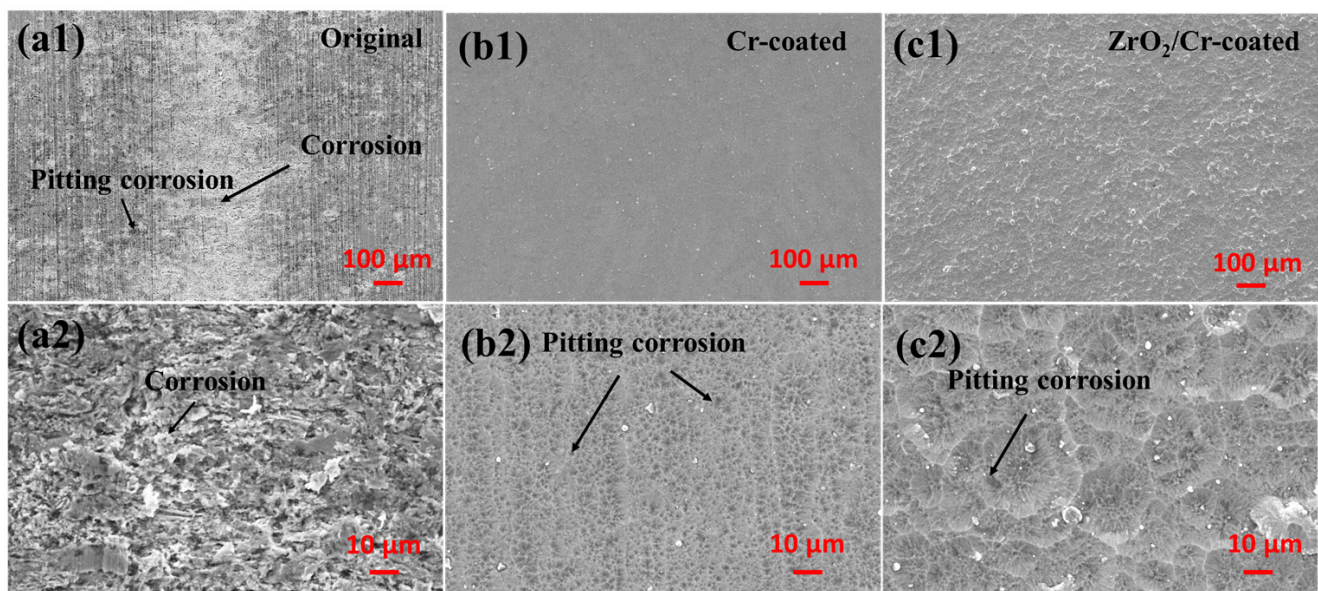
**Figure 5.** Corrosion morphology of the (a1,a2) original, (b1,b2) Cr-coated and (c1,c2) ZrO₂/Cr-coated Zr-4 alloys.

Figure 6 shows the Nyquist and Bode plots of the original and coated Zr-4 alloys in 1200 mg/L H₃BO₃ and 2.2 mg/L LiOH. As shown in Figure 6a, Nyquist curves of the original Zr-4 alloy display smaller capacitive loops compared with those of the coated Zr-4 alloy. A partially enlarged image of Nyquist curves is shown in Figure 6b, which shows a small circle in the range of 1700 to 4800 Ω·cm². Bode plots in Figure 6d suggest that the impedance values of the coated Zr-4 alloy had orders of magnitude higher than those of the original Zr-4 alloy, indicating a larger polarization resistance and better corrosion resistance of the coated Zr-4 alloy. Moreover, Figure 6c shows that the phase angle reached its maximum value at ~700 Hz. The higher phase angle of ZrO₂/Cr-coated Zr-4 alloy indicates the higher corrosion resistance should be attributed to the dense Cr coating and PEO inner layer deposited on the Zr-4 alloy, which is regarded as a double barrier against ion corrosion [25].

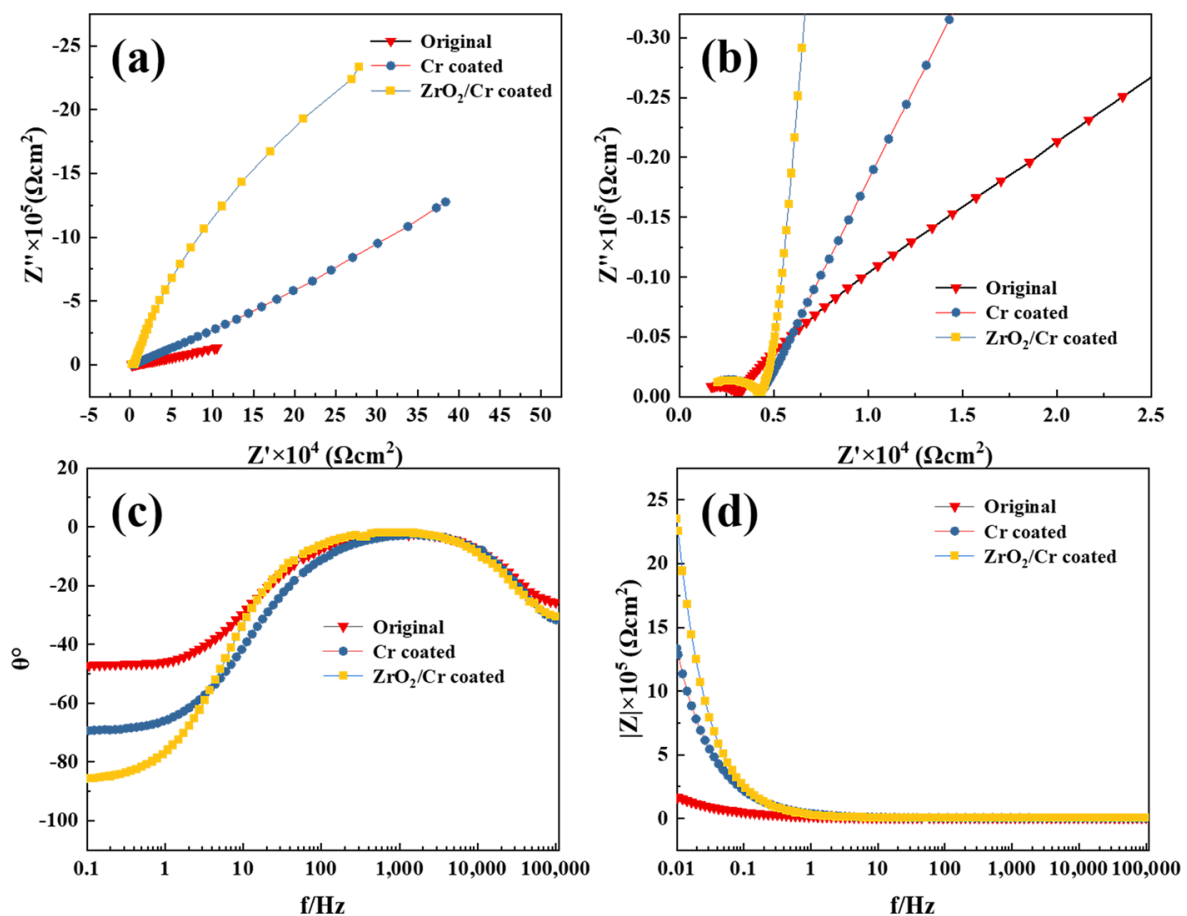


Figure 6. (a) Nyquist, (b) partially enlarged image of Nyquist, (c) Bode Z and (d) Bode phase plots of the original, Cr-coated and ZrO₂/Cr-coated Zr-4 alloys.

The equivalent circuits and physical model of the original, Cr-coated and ZrO₂/Cr-coated Zr-4 alloys were conducted on the basis of electrochemical impedance spectrum data. The fitting results obtained by using ZSimWin software (Version 3.50) are shown in Table 3. Based on the EIS of samples in 1200 mg/L H₃BO₃ and 2.2 mg/L LiOH solution, the equivalent circuit model $R_s(C_{dl}R_{ct})$ was used to simulate the original Zr-4 alloy in solutions (Figure 7a). The model consisted of resistance to the solution (R_s) and charge transfer resistance (R_{ct}) of the Zr-4 alloy, and the C_{dl} represented double electric layer capacitance [26,27]. The equivalent circuit of the Cr-coated Zr-4 alloy is shown in Figure 7b; R_s represents the solution resistance; R_c and C_c are constant phase elements and resistance of Cr coating; and R_{ct} and C_{dl} are charge transfer resistance (R_{ct}) and the double electric layer capacitance of the interface of the Cr coating and Zr-4 alloy. Equivalent circuits of the ZrO₂/Cr composite coating are shown in Figure 7c, comprising R_s , which corresponds to the resistance of the solution; R_c and C_c , which are constant phase elements and resistance of the Cr coating; R_p and C_p , which are resistance and constant phase elements of the PEO porous (outer) layer; and R_{ct} and C_{dl} , which are charge transfer resistance (R_{ct}) and the double electric layer capacitance of the interface of the PEO inner layer and Zr-4 alloy. As shown in Table 3, the R_{ct} of the coated Zr-4 alloy ($9.48 \times 10^8 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^{-n}$ for the Cr-coated Zr-4 alloy and $3.39 \times 10^7 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^{-n}$ for the ZrO₂/Cr-coated Zr-4 alloy) increased by an order of magnitude compared with that of the original Zr-4 alloy ($9.25 \times 10^4 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^{-n}$), which indicates that the dense Cr coating plays an important role in improving the corrosion resistance of the Zr-4 alloy. In addition, as exhibited in Table 3, R_{c1} corresponds to resistance of the PEO porous (outer) layer, providing dual protection for the Zr-4 alloy. Together with Figures 4–6, it can be presumed that ZrO₂/Cr has the most excellent corrosion resistance.

Table 3. Fitted parameters to fit the experimental EIS data of the original, Cr-coated and ZrO₂/Cr coated Zr-4 alloys obtained from polarization curves.

Sample	R_s ($\Omega \text{ cm}^2$)	C_{dl} ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^{-n}$)	n	R_{ct} ($\Omega \text{ cm}^2$)	C_c ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^{-n}$)	N	R_c ($\Omega \text{ cm}^2$)	C_p ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^{-n}$)	n	R_p ($\Omega \text{ cm}^2$)
Original	1177	2.73×10^{-5}	0.61	9.25×10^4	-	-	-	-	-	-
Cr-coated	1066	6.66×10^{-6}	0.79	9.48×10^8	2.36×10^{-7}	0.92	3180	-	-	-
ZrO ₂ /Cr-coated	1109	6.18×10^{-6}	0.97	3.39×10^7	3.5×10^{-9}	0.89	3949	1.54×10^{-6}	0.77	1.61×10^4

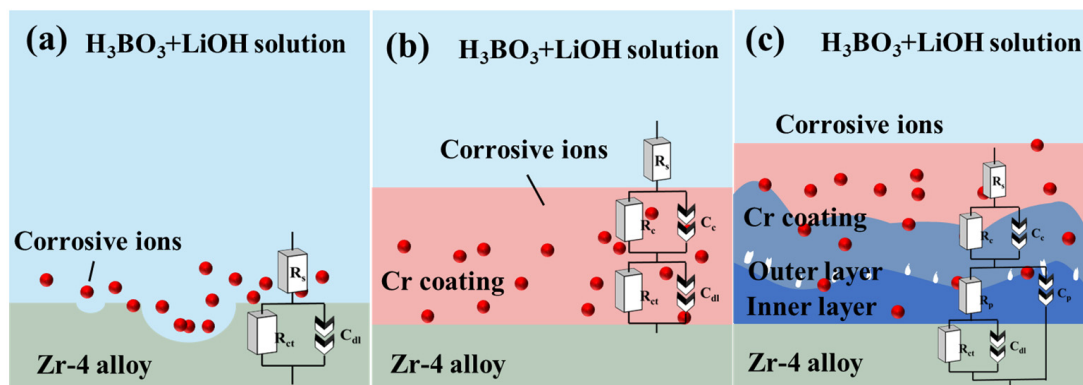


Figure 7. Equivalent circuits and physical model of the (a) original, (b) Cr-coated and (c) ZrO₂/Cr-coated Zr-4 alloys.

3.3. Tribological Performance

The friction–load curves during the scratch test and panoramic view of the scratch groove of the coatings for Cr and ZrO₂/Cr are represented in Figure 8. Obvious cracking and delamination of both coatings under loading forces were observed. As seen in Figure 8a, the values of Lc of the Cr and ZrO₂/Cr coatings were 23.46 and 17.74 N, respectively. The adhesion strength of the coating–substrate is controlled by the hardness, modulus of elasticity, microstructure, composition and thickness [28]. The lower value of Lc of ZrO₂/Cr coatings is ascribed to the high coating porosity of the PEO coating [29].

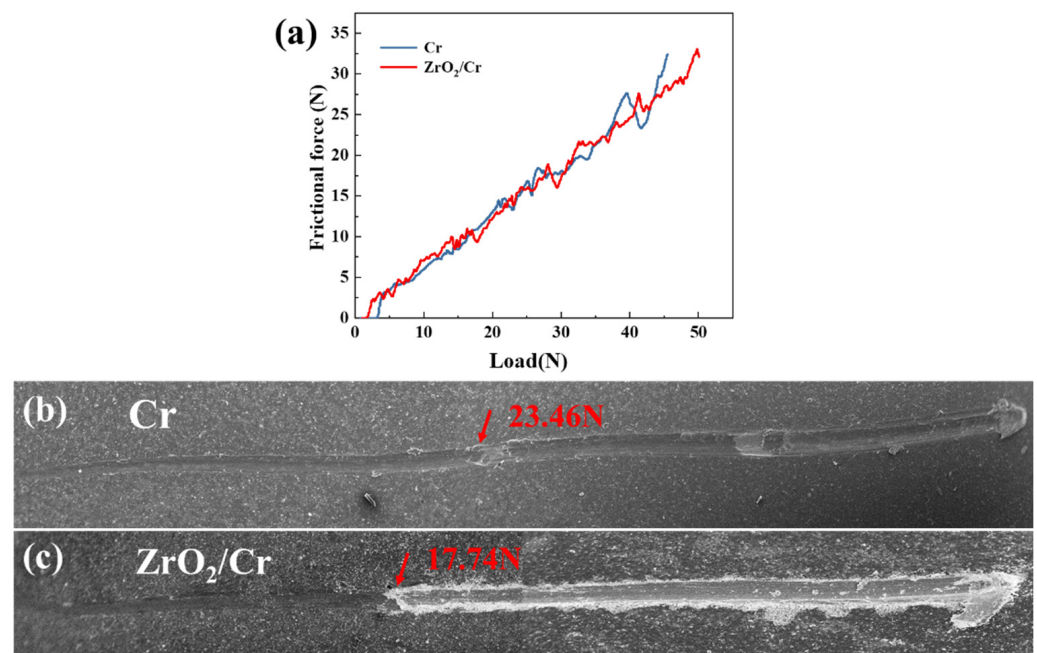


Figure 8. (a) The friction–load curves during the scratch test and (b,c) panoramic view of the scratch groove of the coatings for Cr and ZrO₂/Cr.

Reciprocating friction and wear tests of the original and coated Zr-4 alloys were performed using a multifunctional material surface performance tester (MFT 4000) with a ball-on-disk contact configuration, and the coefficient of friction (COF) of the original and coated Zr-4 alloy is shown in Figure 9a. For the original Zr-4 alloy, there was a rapid increase in the COF at the initial stage, and it stabilized at 0.82. Compared with the original Zr-4 alloy, the COF of the Cr-coated Zr-4 alloy was slightly lower than the original sample due to the increase in hardness [30]. For the ZrO₂/Cr-coated Zr-4 alloy, the friction coefficient decreased significantly, which can be ascribed to stable tetragonal zirconia, which is easily formed on the surface of the Zr alloy in an aluminate electrolyte [31], and the ZrO₂ hard layer plays a good supporting role in the friction and wear process. On the other hand, the deposition of the Cr coating filled the pores of the ZrO₂ coating, making the surface smoother than that of the ZrO₂ coating, and the thickness of the composite coating was much thicker than that of the Cr coating sample (as shown in Figure 3), thus showing superior wear resistance.

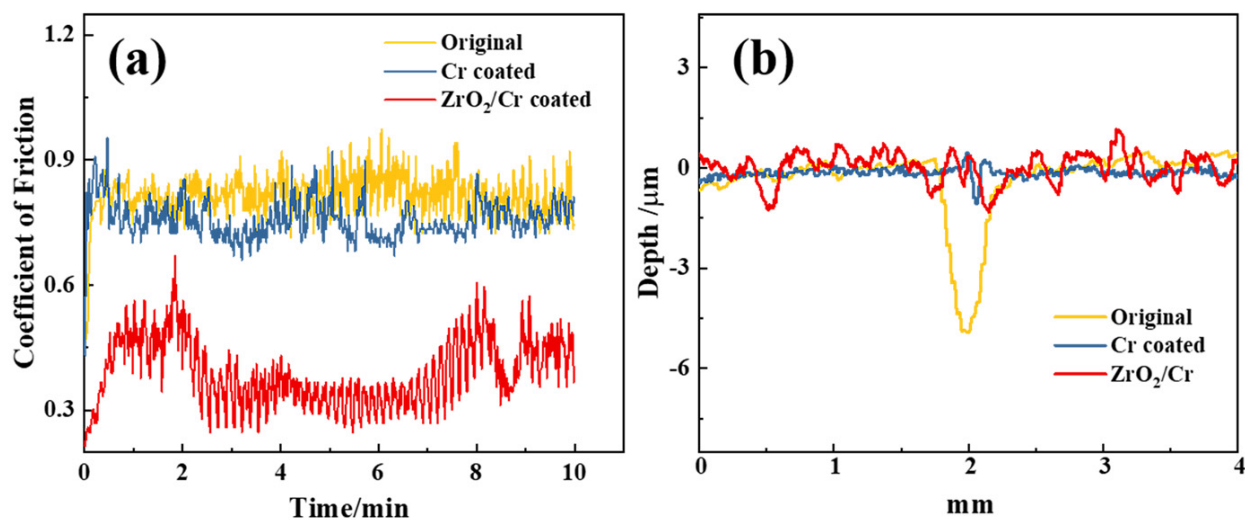


Figure 9. (a) Coefficient of friction and (b) linear wear depth of friction of the original, Cr-coated and ZrO₂/Cr-coated Zr-4 alloys.

From Figure 9b, it can be seen that the wear depth of the Cr-coated Zr-4 alloy was much lower than that of the original Zr-4 alloy. This phenomenon can be attributed to two aspects; on the one hand, the higher hardness of the Cr coating reduced the generation of abrasive wear. From the SEM image of worn surfaces for the original and Cr-coated Zr-4 alloys (Figure 10a,b), it can be seen that the abrasive wear on the worn area of the original samples, furrows and abrasive dust generate can be observed. For the Cr-coated Zr-4 alloy, from the SEM image, serious plastic deformation can be observed in the worn area, but the spalling of the wear debris was not observed. On the other hand, the friction pair composed of the same metal material had a large adhesion tendency and was prone to adhesive wear. The Cr-coated Zr-4 alloy enhanced the adhesive wear resistance through avoiding similar friction pairs [32,33]. It was interesting to observe that the wear depth of the ZrO₂/Cr-coated Zr-4 alloy was difficult to distinguish due to the surface roughness, but it can still be seen that the wear depth was significantly lower than that of the original sample. From the SEM images of the worn surface for the ZrO₂/Cr-coated Zr-4 alloy (Figure 10c), the existence of plastic deformation can be observed, meaning the main wear mechanism is fatigue.

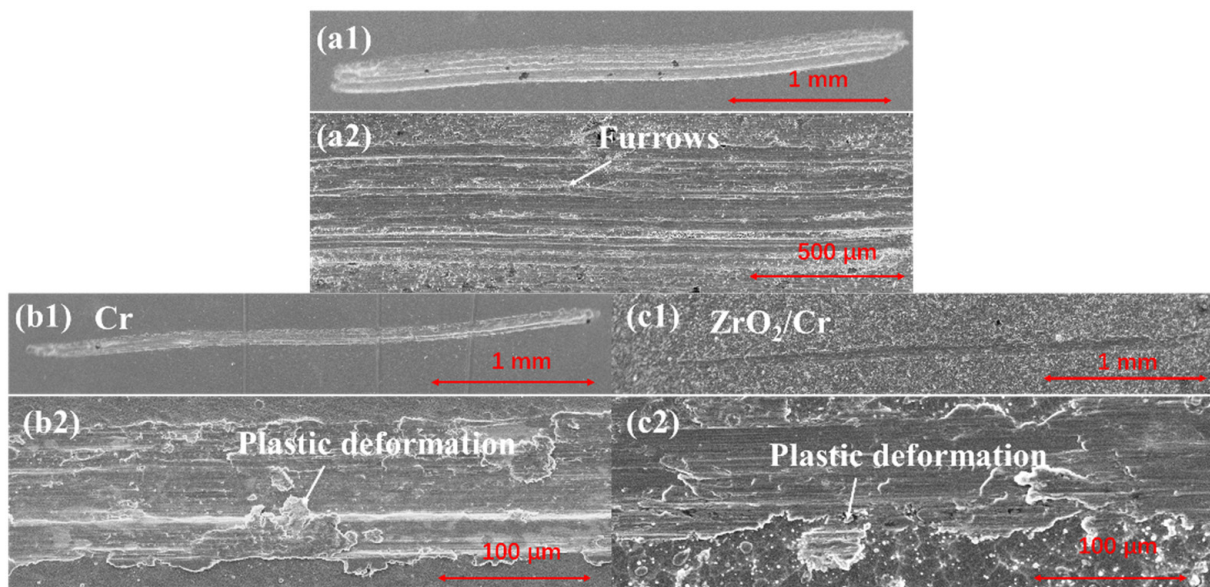


Figure 10. SEM images of worn surfaces for the (a1,a2) original, (b1,b2) Cr-coated and (c1,c2) ZrO_2/Cr -coated Zr-4 alloys.

4. Conclusions

In this study, ZrO_2/Cr bilayer coating was prepared using plasma electrolytic oxidation (PEO) followed by multi-arc ion plating on Zr-4 alloy substrates. Wear and corrosion resistance of Zr-4 alloy with Cr coating and ZrO_2/Cr bilayer coating were evaluated and compared, and the following conclusions can be summarized from this study:

1. Cr and ZrO_2/Cr coatings have similar surface morphology. The more obvious surface undulates on the ZrO_2/Cr coating were due to the rough surface of the PEO coating. Cross-section morphology showed that the thickness of the Cr coating was about $2.6 \mu\text{m}$. The thickness of the ZrO_2/Cr coating was about $15 \pm 1.2 \mu\text{m}$, and it was observed that Cr partly filled in the PEO coating due to the existence of micropores.
2. Pitting corrosion occurred on the surface of the original and coated Zr-4 alloys during the electrochemical corrosion. The ZrO_2/Cr -coated Zr-4 alloy exhibited superior corrosion resistance with an i_{orr} value of $1.86 \times 10^{-6} \text{ A/cm}^2$, which is lesser than that of the Cr-coated Zr-4 alloy with an i_{orr} value of $6.42 \times 10^{-6} \text{ A/cm}^2$ owing to its double-barrier construction and high thickness ($15 \pm 1.2 \mu\text{m}$). The coating on the Zr-4 alloy had better corrosion resistance than that of the original Zr-4 alloy with an i_{orr} value of $1.02 \times 10^{-5} \text{ A/cm}^2$.
3. Critical loads of Cr and ZrO_2/Cr coatings were 23.46 and 17.74 N, respectively, and the lower critical load of ZrO_2/Cr coatings is ascribed to the high coating porosity of the PEO coating. The wear resistance of the coated Zr-4 alloy was enhanced due to the increase in hardness. The wear depth of the coating on the Zr-4 alloy was much lower than that of the original Zr-4 alloy, which is attributed to the change of the wear mechanism from abrasive wear to fatigue wear.

Author Contributions: X.P.: Investigation, Methodology, Writing—Original Draft. L.Q.: Funding acquisition, Writing—Review and Editing, Validation. X.H.: Conceptualization, Writing—Review and Editing. H.J.: Funding acquisition, Formal Analysis, Investigation, Methodology. All authors have read and agreed to the published version of the manuscript.

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