

Article

Study of Wear and Corrosion Resistance of Cold Sprayed TC4 Coating on the Surface of Mg-Li Alloy

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Abstract: Mg-Li alloys have achieved vital applications in aerospace, automotive, and 3C fields for their prominent properties. However, the Mg-Li alloy exhibits poor corrosion and wear resistance due to the high activity of Mg and Li elements and low hardness of Mg. Accordingly, TC4 alloy coating was prepared on the surface of Mg-Li alloy using the cold spray technique to enhance the surface properties. Moreover, the microstructure, microhardness, tribological properties, and corrosion resistance of the coating were systematically investigated. As indicated by the results, the interface between the coating and the Mg-Li alloy substrate was mechanical bonding without significant defects. Several pores exist in the cold sprayed TC4 coating for its high elasticity, toughness, and passivation, resulting in a porosity of 4.3%. The microhardness of the cold sprayed TC4 coating reached 296.3 HV, marking a notable increase in comparison with the substrate. The TC4 alloy coating has better wear resistance than the Mg-Li alloy substrate. The wear volume of the cold sprayed TC4 alloy only accounted for 38% of that of Mg-Li alloy. Abrasive wear was the major wear mechanism of the TC4 alloy coating. In electrochemical tests, the corrosion current density of the TC4 alloy coating (1.426×10^{-5} A/cm²) was two orders of magnitude lower than that of the magnesium-lithium alloy substrate (1.008×10^{-3} A/cm²), and the corrosion potential of the TC4 alloy coating was higher, which indicates that the coating has excellent corrosion resistance.

Keywords: Mg-Li alloy substrate; cold spray; TC4 coating; wear resistance; corrosion resistance



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1. Introduction

Mg-Li alloy has been confirmed as one of the lightest structural materials in the world [1]. It has been extensively employed in aerospace, automotive and 3C fields [1,2] for its several advantages (e.g., low density, high specific strength, shock absorption performance, and resistance to high-energy particle penetration). However, the Mg-Li alloy exhibits poor corrosion resistance due to the high activity of Mg and Li elements [3]. In addition, it exhibits poor wear resistance due to severe adhesive wear arising from its lower hardness [4]. Thus, researchers proposed to address the above problems using surface protection technology, such as preparing protective coatings on the surface of Mg-Li alloys that are capable of avoiding direct contact between the substrate and the external environment, enhancing the corrosion resistance and wear resistance of the substrate surface, and contributing to the extension of the service life of the substrate and the lowering of usage costs [5,6]. Conventional surface protection technologies for Mg-Li alloys include anodic oxidation [7], microarc oxidation [8], electroless plating [9], chemical conversion [10], etc. Conventional surface protection techniques provide insufficient protection for Mg-Li alloys, and there are still some issues that need to be addressed, such as the unclear coating formation mechanism, environmental pollution problems, and relatively thin coating thickness, etc.

Cold spray technology refers to a solid-state process exhibiting a high spray rate and deposition efficiency [11]. Compared to thermal spray techniques, cold spray techniques are effective in preventing grain growth, phase transformation, and coating oxidation due to the lower working environment temperature, thus contributing to the production of dense coatings for oxidation-sensitive and heat-sensitive materials [12]. Moreover, due to its non-melting powder characteristic, cold spraying has very little thermal impact on the substrate, so low melting point substrates, such as magnesium alloy and aluminum alloy, will not be diluted or damaged during the cold spraying process [13]. Accordingly, cold spraying technology has great potential application value for improving the wear resistance and corrosion resistance of the Mg-Li alloy.

Titanium and titanium alloys have advantages such as high specific strength, plasticity, and corrosion resistance, making them commonly used for cold spray coating materials [14]. Daroonparvar et al. [15] significantly improved the corrosion resistance of an AZ31B magnesium alloy by depositing a Ti/Ta coating and a cold sprayed Al coating on the surface of the AZ31B magnesium alloy. Khun et al. [16] deposited a TC4 coating with the thickness of 9 mm on a TC4 substrate using a high-pressure cold spraying process, and it was found that the TC4 coating had higher hardness and similar wear resistance in comparison with the substrate. Sun et al. [17] deposited a TC4 coating on a 6061-T651 aluminum alloy substrate using the cold spraying process, which improved the wear and corrosion resistance. Existing investigations have shown that cold spraying titanium or titanium alloy can enhance the wear resistance and corrosion resistance of the alloy surface. Based on this, cold spraying a titanium alloy coating on the surface of Mg-Li alloy may enhance its wear resistance and corrosion resistance.

There are currently few reports on cold spraying on Mg-Li alloy surfaces. In this study, a wear and corrosion resistant coating with prominent performances was prepared on the surface of Mg-Li alloy by combining the prominent properties of TC4 titanium alloy and the advantages of cold spraying technology. The microstructure of the coating and the properties of the coating were also systematically analyzed. This study provides a useful theoretical reference as well as an empirical reference for the surface protection of Mg-Li alloy.

2. Materials and Methods

TC4 alloy, prepared using the atomization method by Ningbo Zhongyuan New Materials Technology Co., Ltd. (Ningbo, China) was selected as the cold spraying powder. The morphology and size distribution of TC4 titanium alloy powder are shown in Figure 1. The size distribution of the powder was measured by a laser particle analyzer (Mastersizer 2000, Malvern, UK). As depicted in the figure, the particles were mostly spherical or nearly spherical with an average size of 12.71 μm . The spherical particles with high fluidity contributed to the uniform feeding of the powder into the deposition in the spraying process. The substrate material chosen was Mg-Li alloy, and the size of the specimen was 150 mm $\times$ 58 mm $\times$ 8 mm. Table 1 lists the compositions of the Mg-Li alloy and the TC4 powder. The TC4 titanium alloy coatings on the surface of the Mg-Li alloy were prepared using a high-pressure cold spray system (Impact Innovations GmbH, Rattenkirchen, Germany). Before cold spraying, to ensure the high flow ability of the powder, the TC4 powder was heated in a vacuum drying oven at 100 $^{\circ}\text{C}$. Subsequently, sandpaper was used to polish the surface of the substrate until it was flat. The sample was immersed in anhydrous ethanol for ultrasonic cleaning for 20 min to avoid impurities (e.g., oil stains affecting the experimental results). Lastly, the Mg-Li alloy sample was sandblasted. Sandblasting treatment can rough up the surface of the substrate, which is helpful to enhance the bonding strength between the TC4 powder and the magnesium-lithium alloy. The TC4 powder particles were deposited smoothly at a critical speed by combining the melting point and flow ability of TC4 titanium alloy [18]. With the coating porosity as the coating quality evaluation index, the process parameters for cold spraying with the minimum coating porosity were determined through multiple tests, comprising a carrier gas pressure of

39 bar, a carrier gas temperature of 780 °C, a powder feeding speed of 3 r/min, a spraying distance of 25 mm, as well as a nitrogen protection gas flow rate of 80 m³/h.

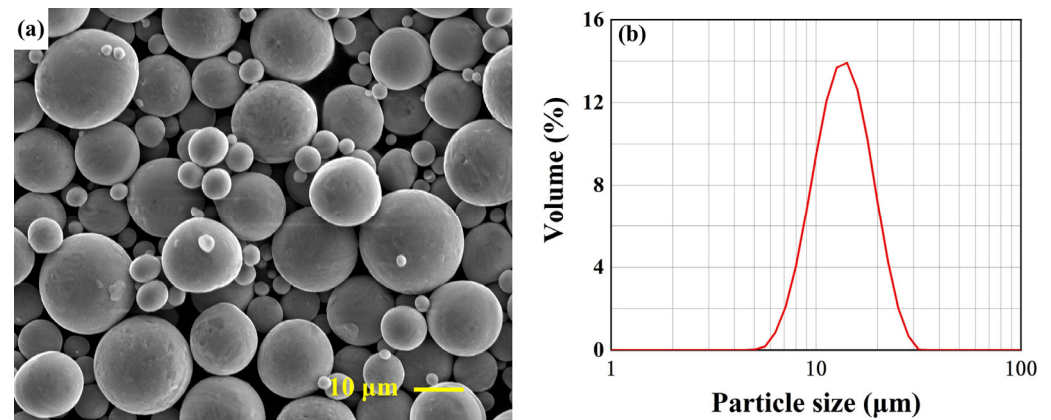


Figure 1. Morphology and particle size distribution of TC4 titanium alloy powder: (a) SEM image, and (b) particle size distribution.

Table 1. Chemical composition of the Mg-Li alloy and TC4 powder (wt.%).

Composition	Li	Zn	Y	Mg	V	Al	Ti
Mg-Li alloy	8.03.	4.94	0.73	Bal	-	-	-
TC4 powder	-	-	-	-	4	6.09	Bal

The phase composition of the coating and substrate was characterized using an X-ray diffractometer (XRD, Rigaku, Akishima, Japan). The target was Cu K α , and the tube voltage was 40 kV. The morphology and elemental composition on the surface and cross-section of the coating were observed using a JSM-6510A scanning electron microscope (SEM, JEOL, Tokyo, Japan) fitted with an energy dispersive spectrometer (EDS). The porosity of the TC4 coating was determined using Image Pro Plus software (Media Cybernetics, Rockville, MD, USA). For the accuracy of the data, three areas were randomly selected at each of the top, middle and bottom positions of the coating cross-section and their SEM images were examined at 1000 $\times$, and the average value determined was the porosity of the coating.

The microhardness of the coating was examined by a HMV-2000 Vickers hardness tester (Shimadzu, Kyoto, Japan) with a load of 1.96 N for 15 s. To reduce experimental errors, the measurement was performed five times in parallel at the respective test point, and the average value was employed as the final test result. The wear test was conducted on a UMT-3 wear tester (CETR, Campbell, CA, USA) at ambient temperature. A Si₃N₄ grinding ball with a radius of 3 mm was selected as the friction pair. The following test parameters were selected: the sliding length of 4 mm, the load of 5 N, the frequency of 2 Hz, and the test time of 20 min. To ensure the flatness of the sample and improve the accuracy of the test, the specimen surface was mechanically polished, and alcohol ultrasonic cleaned and dried prior to the test. After the wear test was performed, the wear scars were scanned using a MicroXAM-3D surface profiler (ADE, San Jose, CA, USA) to determine the wear volume of the substrate and the TC4 coatings.

Electrochemical testing of the Mg-Li alloy and the TC4 alloy coating were performed on an electrochemical workstation (CHI 660, Shanghai Chenhua Instrument Co., LTD, Shanghai, China) using a three-electrode system: a saturated calomel electrode (SCE) as the reference electrode, a platinum electrode as the auxiliary electrode, and the testing specimen as the working electrode. The test temperature reached 25 $\pm$ 3 °C. The tests were performed in 3.5 wt.% NaCl solution. The specimens were closed with cold mounting powder where 1 cm² was exposed. The test time of the open-circuit potential reached 1800 s. The AC impedance spectrum was examined from 10⁻² to 10⁵ Hz with an amplitude of 5 mV. The starting and ending potentials of the polarization curve were $\pm$ 0.5 V of the

open-circuit potential, and the sensitivity was 10^{-3} . The polarization curves were fitted in the Tafel region based on the special analysis software that came with the electrochemical workstation, and the electrochemical impedance was fitted with the Zsimp win software (AMETEK Scientific Instruments, Berwyn, IL, USA).

3. Results

3.1. Surface Morphology and Microstructure

Figure 2a presents the original surface of the cold sprayed TC4 alloy coating. As depicted in Figure 2a, the surface of the coating was concave and uneven. It is generally known that a significant plastic deformation occurs when the spherical TC4 alloy particles are subjected to a high-speed impact, and it is easy to produce the mechanical bonding and achieve the interlocking effect [19]. However, some TC4 alloy particles on the outermost layer of the coating are not subjected to plastic deformation, and they still display a spherical shape. The reason for this is that some particles had been accelerated to the critical velocity without obtaining sufficient thermal energy to fully soften. Moreover, the surface particles lacked the tamping effect of the subsequent particles [20]. Figure 2b shows the cross-sectional morphology of the cold sprayed TC4 coating. As depicted in the figure, the thickness of the coating was approximately 586 μm , and the interface between the coating and the Mg-Li alloy substrate was wavy without significant defects. The soft Mg-Li alloy substrate was deformed seriously after suffering the impact of hard TC4 alloy particles, thus causing the wavy interface. Moreover, the TC4 alloy powder impacted the Mg-Li alloy substrate at such a high speed that local heating and plastic deformation of the substrate were caused. Besides, the oxide layer broke and cracked under impact and the exposed fresh metal bonded to each other to produce a mechanical interlocking [21]. Figure 2c shows the high-magnification view of the cross-section of the cold sprayed TC4 alloy coating. As depicted in the figure, some pores appeared in the coating. In the cold spray process, some TC4 alloy particles were not deformed sufficiently, and failed to form an effective bond, resulting in the porosity of 4.3%.

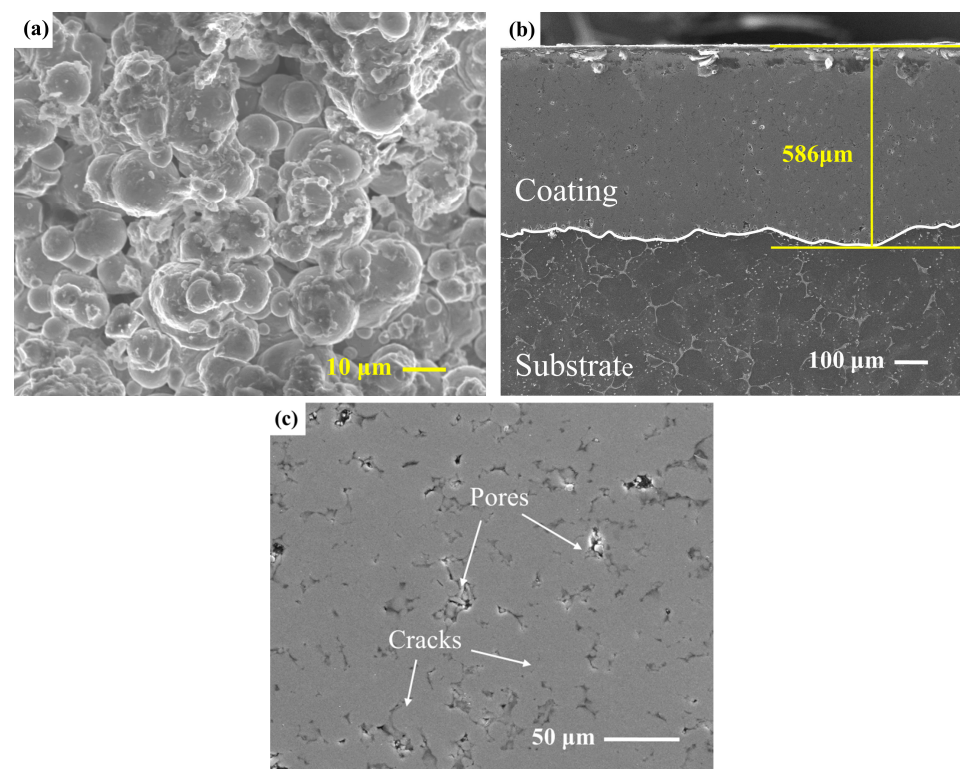


Figure 2. Surface morphology of TC4 coating (a), and cross-sectional morphologies of TC4 coating (b,c).

The elements distribution throughout the interface between the coating and substrate is shown in Figure 3a. The absence of Ti, Al, and V elements in the substrate, as well as the absence of Mg elements in the TC4 coating, further confirmed that the bonding mode between the TC4 coating and the Mg-Li alloy substrate was mechanical bonding [22]. Figure 3b shows the bonding morphology of the TC4 coating and the Mg-Li alloy matrix at high magnification. It can be found that no other intermetallic compounds exist between the Mg-Li alloy and the TC4 coating. The reason for this result is that there is no intermetallic compound between the Mg-Li alloy matrix and the main elements of the TC4 titanium alloy coating, Ti and Mg, and the solid solution degree is very small, such that a metallurgical bond between the TC4 coating and the Mg-Li alloy is difficult to form.

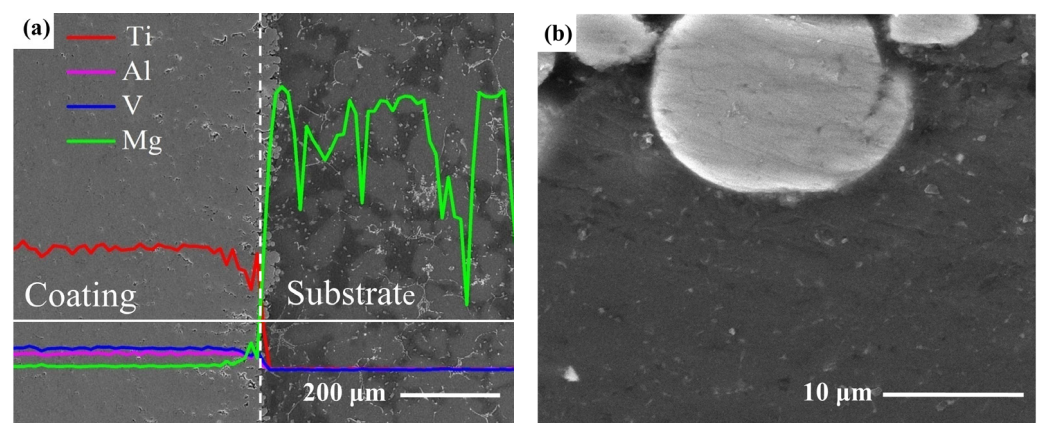


Figure 3. Elemental distribution curves of the interface between the coating and substrate (a); interface morphology between coating and substrate (b).

Figure 4 presents the XRD patterns of the TC4 powder and the cold sprayed coating. It can be seen that all the diffraction peaks of the TC4 powder and the coating are well matched with the α -phase, and no other phases were detected. This indicates that the sprayed particles did not undergo phase transformation or oxidation during the cold spraying process, which exhibits the unique benefits of the cold spraying process [23].

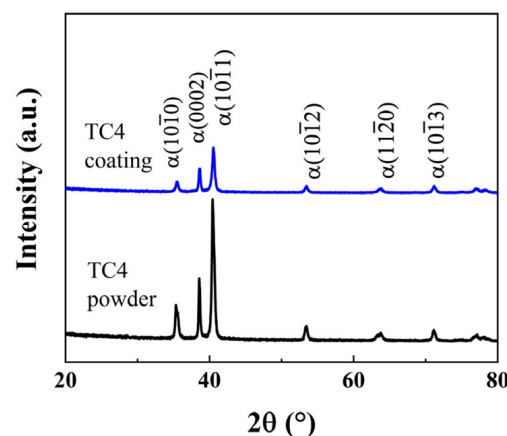


Figure 4. XRD patterns of the TC4 powder and cold sprayed TC4 coating.

3.2. Microhardness and Tribological Properties

Figure 5 presents the microhardness distribution at the interface between the cold sprayed TC4 coating and the Mg-Li alloy substrate. As depicted in the figure, the average hardness of the substrate and the cold sprayed TC4 coating reached 68.7 and 296.3 HV_{0.2}, respectively. The coating exhibited higher hardness than the substrate. Moreover, a slight increase was reported in hardness from the Mg-Li alloy substrate to the interface. The reason for this result is the reinforcing effect of particle impact during the cold spraying

process [24]. For the coating, the hardness near the interface becomes greater due to the deformation at high strain rates and the hardening that occurs during the process of deposition of the cold sprayed particles. Furthermore, Boruah et al. suggested that the surface residual compressive stresses, combined with the tamping effect of the subsequent particles, increased the hardness of the coating [25].

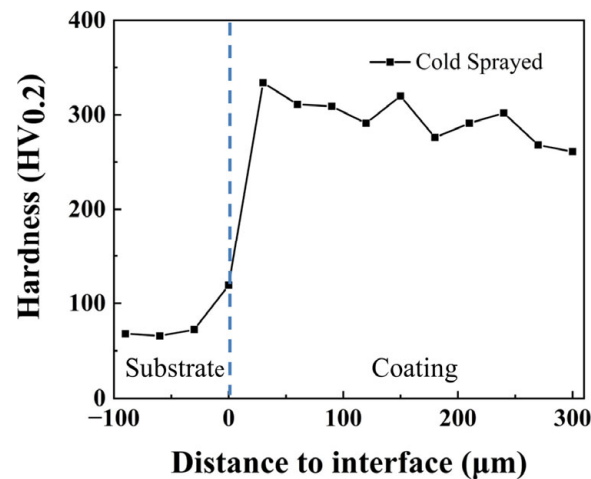


Figure 5. Microhardness distribution of the interface between the cold sprayed TC4 coating and the Mg-Li alloy substrate.

Figure 6 presents the friction coefficient of the substrate and the cold sprayed TC4 alloy coating with different sliding times. As depicted in the figure, it can be observed that the friction coefficient of the Mg-Li alloy substrate tended to be stabilized into the stable wear stage after the early run-in wear stage, and it was finally stabilized around 0.38. At the beginning of wear, the rough material surface, the smaller actual contact area, and the higher contact stress resulted in a higher coefficient of friction. After a period with the contact point under the action of shear plastic flow, the higher micro-convex body tended to be reduced, such that the actual contact area between the friction pairs was increased until it achieved a relatively stable state, and the friction coefficient tended to be stable. The friction coefficient of the cold sprayed TC4 coating was finally stable around 0.53 after the run-in period. The low hardness of the Mg-Li alloy resulted in a low shear strength, thus endowing the Mg-Li alloy with a lower friction coefficient than the TC4 coating.

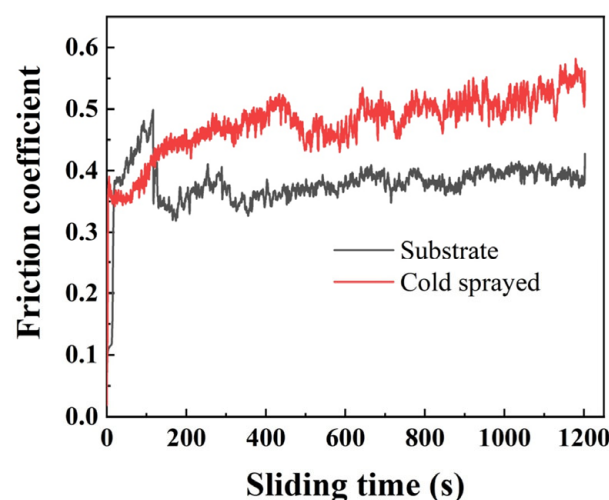


Figure 6. Friction coefficient curves of the Mg-Li alloy substrate and the cold sprayed TC4 alloy coating.

Figure 7 presents the three-dimensional topography and dimension information of the worn surfaces of the Mg-Li alloy substrate and TC4 alloy coating under the same friction test conditions. As depicted in the figure, the wear scar profile of the Mg-Li alloy substrate was deep and wide, and the maximum depth and width of the scars reached $52.9\ \mu\text{m}$ and $1.25\ \text{mm}$, respectively, with the wear volume of $0.121\ \text{mm}^3$. The wear scar profile of the cold sprayed TC4 alloy coating was shallower and narrower, with a maximum depth and width of $25.8\ \mu\text{m}$ and $0.94\ \text{mm}$ and a wear volume of $0.046\ \text{mm}^3$. Although the friction coefficient of the Mg-Li alloy substrate was smaller, the wear volume of the coating was 38% of the substrate. The reason for this result is that the cold sprayed TC4 alloy coating exhibits a higher hardness in comparison with the Mg-Li alloy substrate. According to Archard's law, the amount of wear is inversely proportional to the hardness of the wear surface [26]. The cold sprayed TC4 alloy coating surface has a greater hardness than the Mg-Li alloy substrate surface, giving it a smaller amount of wear than the Mg-Li alloy substrate during the friction process. The cold sprayed TC4 alloy coating exhibited better wear resistance while providing better protection for the Mg-Li alloy substrate.

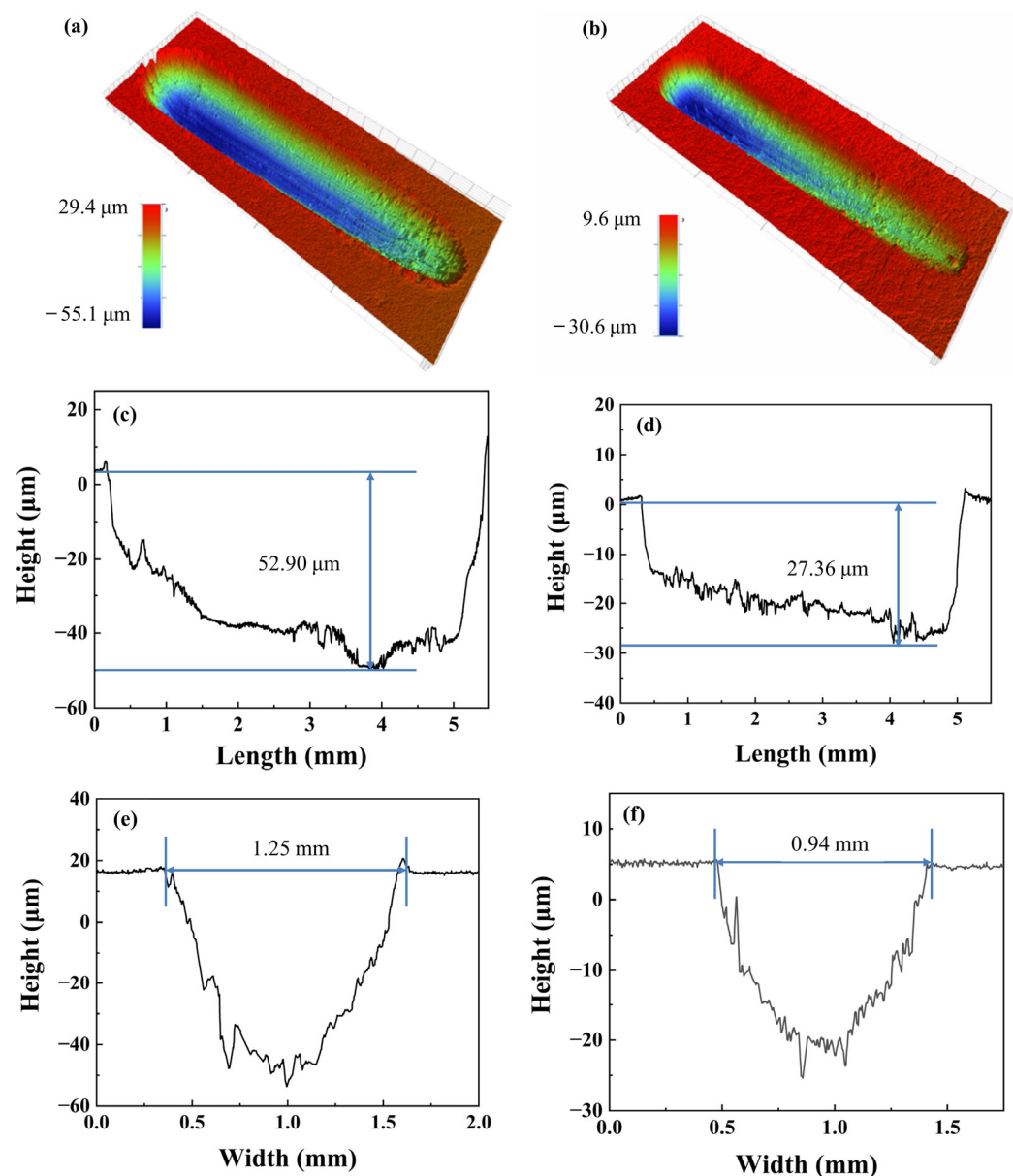


Figure 7. 3D topography of the worn surfaces and the typical wear scar size: (a,c,e) Mg-Li alloy substrate; (b,d,f) TC4 alloy coating.

Figure 8 presents the wear surface topography of the Mg-Li alloy substrate. As depicted in Figure 8a,b, the wear mechanism of the Mg-Li alloy substrate was mainly adhesive wear, accompanied by fatigue wear, as well as abrasive wear. The Mg-Li alloy exhibited lower hardness, and it was prone to compression, plastic deformation, and adhesion to the grinding ball during the friction process. Thus, during the continuous sliding process, the adhesion points were sheared and then transferred to form spalling pits, suggesting the presence of adhesive wear [27]. The appearance of furrows in Figure 8a confirmed the presence of abrasive wear [28]. Moreover, the spalling pits formed by crack propagation under alternating loads were evidence of fatigue wear. Figure 8c presents the O element map scanning analysis in Figure 8a. As depicted in the figure, the O element in the worn zone was significantly higher than that in the non-worn zone, suggesting that the Mg-Li alloy can produce more oxides during the friction process.

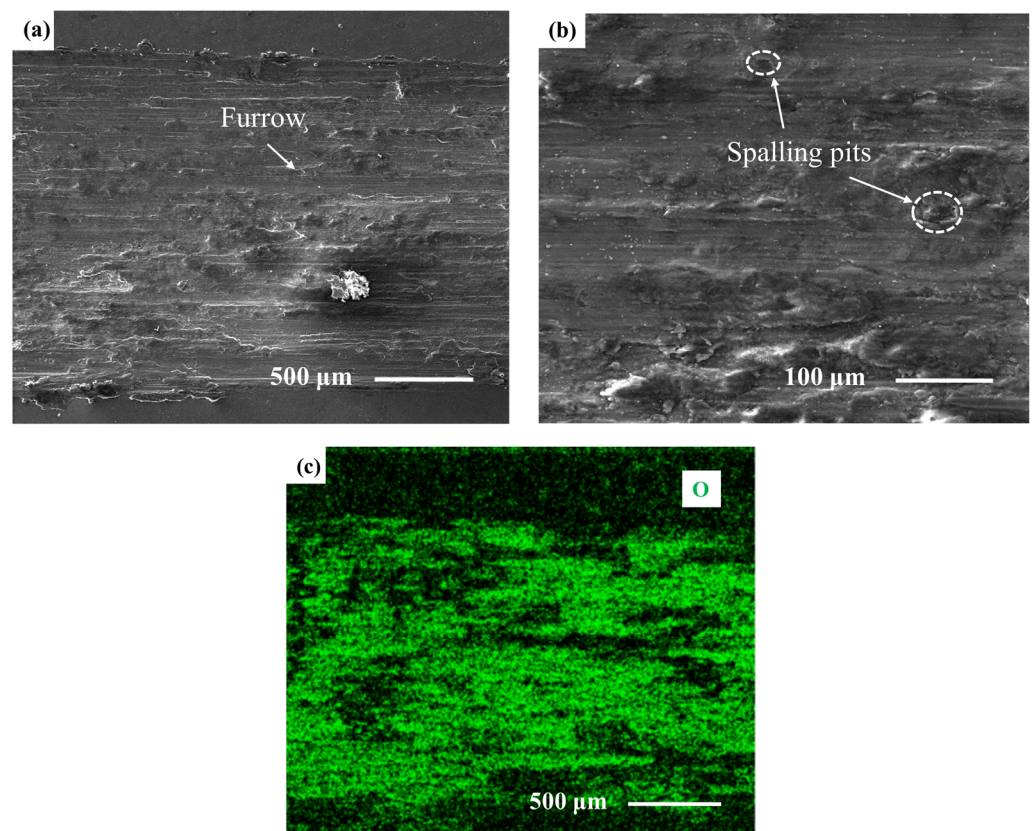


Figure 8. Morphologies of the worn surfaces of the Mg-Li alloy substrate: (a,b) SEM morphologies, and (c) O element map scanning analysis of Figure 8a.

Figure 9 shows the worn surface morphology of the cold sprayed TC4 alloy coating. As depicted in Figure 9, the wear mechanism of the TC4 alloy coating was primarily abrasive wear, accompanied by fatigue wear and adhesive wear. The worn scars displayed typical adhesion marks and furrow characteristics [29]. In the sliding process, the alternating loads induced plowing and plastic tearing of the TC4 alloy, thus resulting in material peeling and the formation of abrasive debris, which gradually wears into smaller abrasive particles. Figure 9c shows the O element map scanning analysis of Figure 9a. It can be observed that the O element was evenly distributed on the worn surfaces, and no special oxides were found.

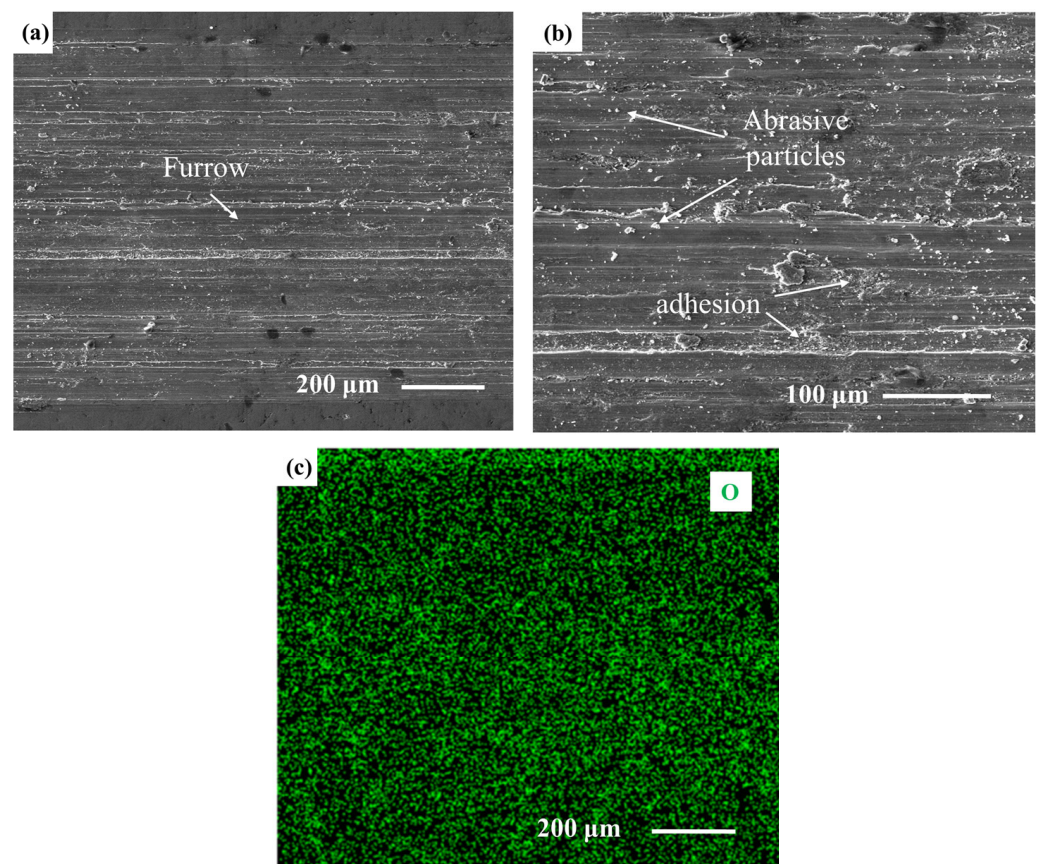


Figure 9. Morphologies of the worn surfaces of the TC4 alloy coating: (a,b) SEM morphologies, and (c) O element map scanning analysis of Figure 9a.

The difference in hardness makes the Mg-Li alloy prone to adhesive wear, resulting in extensive peeling of the material, while the TC4 alloy coating is more inclined to abrasive wear and less likely to cause extensive spalling. Accordingly, the TC4 alloy coating has better wear resistance and can effectively protect the Mg-Li alloy substrate.

3.3. Corrosion Properties

The polarization curves of the Mg-Li alloy substrate and the TC4 alloy coating are shown in Figure 10a. It can be clearly observed that the TC4 alloy coating had a larger corrosion potential (E_{corr}) and a lower corrosion current density (i_{corr}). The corrosion potential and corrosion current density of the Mg-Li alloy substrate and cold sprayed TC4 alloy coating were calculated by fitting the polarization curves through the electrochemical workstation, as presented in Table 2. The corrosion potentials of the substrate and TC4 alloy coating are -1.659 and -0.334 V, respectively. The corrosion potential of the TC4 alloy coating is significantly positively shifted with respect to the Mg-Li alloy substrate. The corrosion current density of the Mg-Li alloy substrate and the cold sprayed TC4 alloy coating are $1.008 \times 10^{-3} \text{ A}\cdot\text{cm}^{-2}$ and $1.426 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$, respectively. The corrosion current density of the cold sprayed TC4 alloy coating was two orders of magnitude lower than that of the Mg-Li alloy substrate. Generally, the higher the corrosion potential and the lower the corrosion current density, the stronger the corrosion resistance of the material [30,31]. Thus, the cold sprayed TC4 alloy coating has better corrosion resistance than the Mg-Li alloy substrate, and it can provide good protection to the Mg-Li alloy substrate.

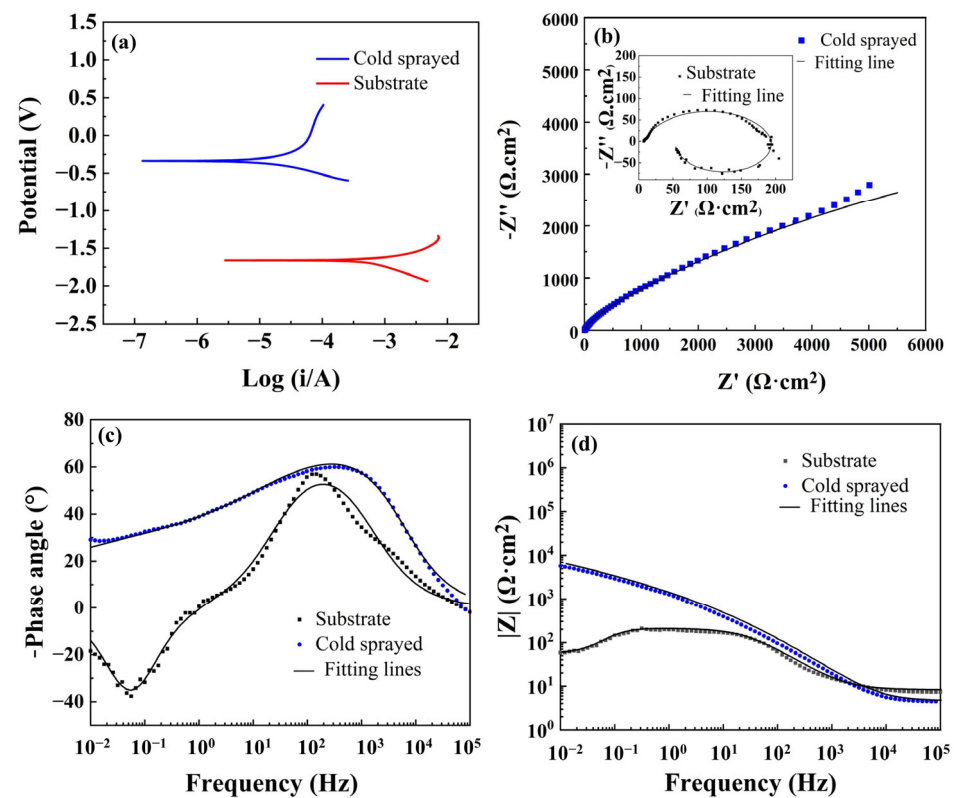


Figure 10. Electrochemical test results of the Mg-Li alloy substrate and cold sprayed TC4 alloy coating: (a) Polarization curves, (b) Nyquist plot, (c) phase-frequency plots, and (d) Bode plots.

Table 2. Polarization curve parameters of the Mg-Li alloy and TC4 alloy coating in 3.5 wt.% NaCl solution.

Specimens	$i_{\text{corr}}/\text{A} \cdot \text{cm}^{-2}$	$E_{\text{corr}}/\text{V}_{\text{SCE}}$
Mg-Li alloy	1.008×10^{-3}	−1.659
TC4 alloy coating	1.426×10^{-5}	−0.334

To gain more insights into the corrosion behavior of the Mg-Li alloy substrate and cold sprayed TC4 alloy coating, the electrochemical impedance spectrum (EIS) was examined at a stable open circuit potential, and the results are presented in Figure 10b–d. As depicted in Figure 10b, the Mg-Li alloy substrate displayed a high frequency capacitive ring and a low frequency inductive ring, whereas the cold sprayed TC4 alloy coating achieved only one capacitive ring. The formation of low-frequency inductive rings was correlated with the conversion and adsorption of substances in the oxide layer, thus taking on critical significance in the protection. The diameter of the capacitance ring in the high frequency region indicates that the impedance was caused by the charge transfer at the interface between the electrolyte and the electrode, and that the larger the radius of the capacitance arc, the greater the charge transfer resistance and the smaller the metal dissolution rate [32]. Obviously, the cold sprayed TC4 alloy coating exhibited a larger radius of tolerance to the capacitance arc, suggesting the better corrosion resistance. Figure 10c presents the Bode phase angle diagram of the Mg-Li alloy substrate and the cold sprayed TC4 alloy coating. As depicted in the figure, the cold sprayed TC4 alloy coating displayed larger phase angle peaks and peak widths, suggesting greater impedance and better corrosion resistance of the coating. The impedance values in the low frequency region in Figure 10d reflect the degree of penetration of the corrosive liquid into the coating [33]. The higher the impedance value in the low frequency region, the more resistant it was to the penetration of the corrosive solution, suggesting that the TC4 alloy coating had superior corrosion resistance.

Figure 11 presents the equivalent circuit model based on the results of Nyquist and Bode plot fitting to quantify the impedance values of the specimens. The electrochemical impedance spectra of the Mg-Li alloy substrate and the cold sprayed TC4 alloy coating were fitted using Zsimp win software (AMETEK, Berwyn, PA, USA) (version v3.60). The equivalent circuits of the Mg-Li alloy substrate and the cold sprayed TC4 alloy coating comprised $R_s(Q_t R_t(LR_l))$ and $R_s(Q_c(R_c(Q_t R_t)))$, respectively. In Figure 11, R_s denotes the solution resistance, R_c represents the passivation film resistance, R_t represents the charge transfer resistance of the Mg-Li alloy substrate or the cold sprayed TC4 alloy coating, Q_c expresses the electrical layer capacitance at the interface between the passivation film and the solution, Q_t represents the double layer capacitance, L is the inductance, and R_l is the inductive resistance. Table 3 lists the specific parameters values of the fitting results. The corrosion performance of the specimen was correlated with R_t ; the larger the value of R_t , the lower the corrosion rate [34]. The R_t of the cold sprayed TC4 alloy coating and the Mg-Li alloy substrate reached 2.36×10^4 and $1.90 \times 10^2 \Omega \cdot \text{cm}^2$, respectively. Furthermore, the R_t of the cold sprayed TC4 alloy coating was two orders of magnitude higher than that of the Mg-Li alloy substrate, suggesting that the cold sprayed TC4 coating exhibited better corrosion resistance.

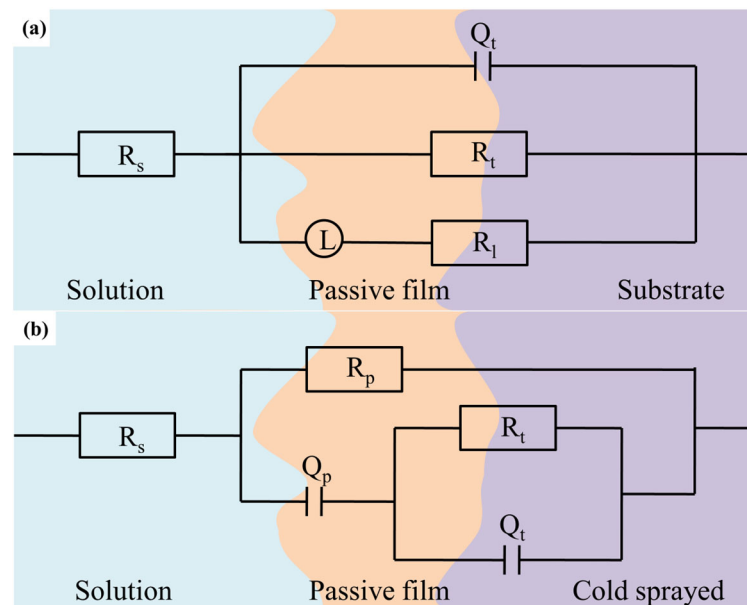


Figure 11. Equivalent circuits used for fitting the EIS: (a) Mg-Li alloy and (b) cold sprayed TC4 alloy coating.

Table 3. Electrochemical parameters of the fitting equivalent circuit.

Specimen	$R_s(\Omega \cdot \text{cm}^2)$	$\frac{Q_c - Y_0}{(\Omega^{-1} \text{cm}^{-2} \text{s}^{-n})}$	Q_c^{-n}	$R_c(\Omega \cdot \text{cm}^2)$	$\frac{Q_t - Y_0}{(\Omega^{-1} \text{cm}^{-2} \text{s}^{-n})}$	Q_t^{-n}	$R_t(\Omega \cdot \text{cm}^2)$	$L(\text{H} \cdot \text{cm}^2)$	$R_l(\Omega \cdot \text{cm}^2)$
Substrate	7.63	8.49×10^{-5}	-	-	-	8.07×10^{-1}	1.90×10^2	3.62×10^2	5.90×10^1
TC4 coating	3.82	3.42×10^{-4}	3.66×10^{-1}	5.01×10^{-1}	3.50×10^{-5}	8.34×10^{-1}	2.36×10^4	-	-

Figure 12 presents the corrosion microscopic morphologies of the Mg-Li alloy substrate and the cold sprayed TC4 alloy after the electrochemical test was performed. As depicted in the figure, the surface of the Mg-Li alloy produced a rough layer of corrosion products under the effect of the localized corrosion. In addition, considerable cracks formed on the surface of the Mg-Li alloy, and the extension and crossover of the cracks led to cracking and spilling of the substrate surface [35]. The 3.5 wt.% NaCl solution had already produced significant damage to the substrate surface. Figure 12c,d presents the EDS pattern of the surface of the Mg-Li alloy after the electrochemical test; it can be seen that the corrosion product surface is enriched with considerable O elements and almost no Mg elements,

which is because the potential of β -Li in the two phases inside the Mg-Li alloy is lower than that of α -Mg phase, and the corrosion occurs preferentially on the β -Li phase, forming the corrosion product LiOH, which cannot be characterized by EDS because the X-Ray energy of Li elements is very weak.

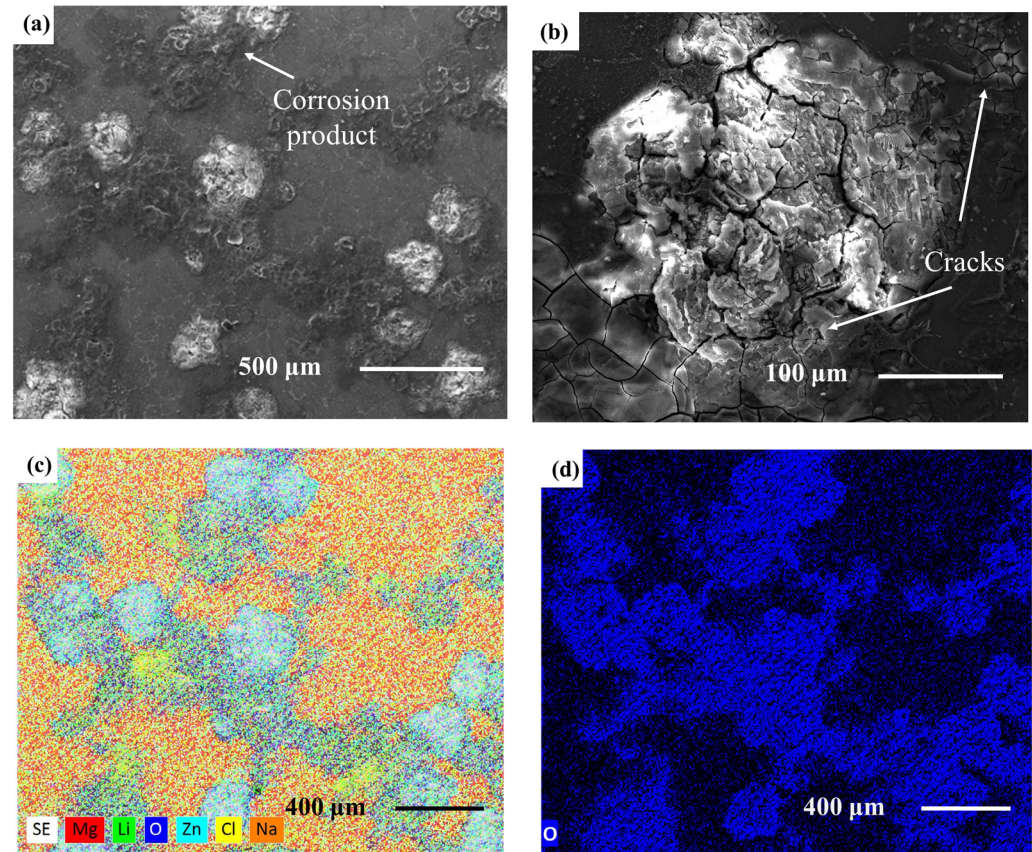


Figure 12. Morphologies of the corrosion of the Mg-Li alloy substrate: (a,b) SEM morphologies, and (c,d) EDS analysis of Figure 12a.

Figure 13 presents the corrosion micromorphology of the cold sprayed TC4 alloy coating after electrochemical testing and the EDS pattern. The overall smooth surface of the cold sprayed TC4 alloy coating did not show any significant corrosion products, and only the chimeras of TC4 particles and the pores between them were identified, suggesting that the coating can effectively resist the corrosion of 3.5 wt.% NaCl solution. As depicted in Figure 13c,d, the overall distribution of elements on the surface of TC4 coating was uniform and there was no significant element enrichment, suggesting that the passivation film was dense and complete and effectively protected the substrate. The surface of the cold sprayed TC4 coating contained considerable O elements since the Ti elements in the TC4 coating rapidly generated a TiO_2 passivation film in the oxygen-containing environment. TiO_2 exhibited an extremely prominent corrosion resistance in the seawater environment, such that the TC4 coating effectively resisted the corrosion of 3.5 wt.% NaCl solution. The TC4 coating on the surface of Mg-Li alloy avoided the direct contact between the substrate and the external corrosive environment, such that the surface corrosion resistance of Mg-Li alloy was effectively improved.

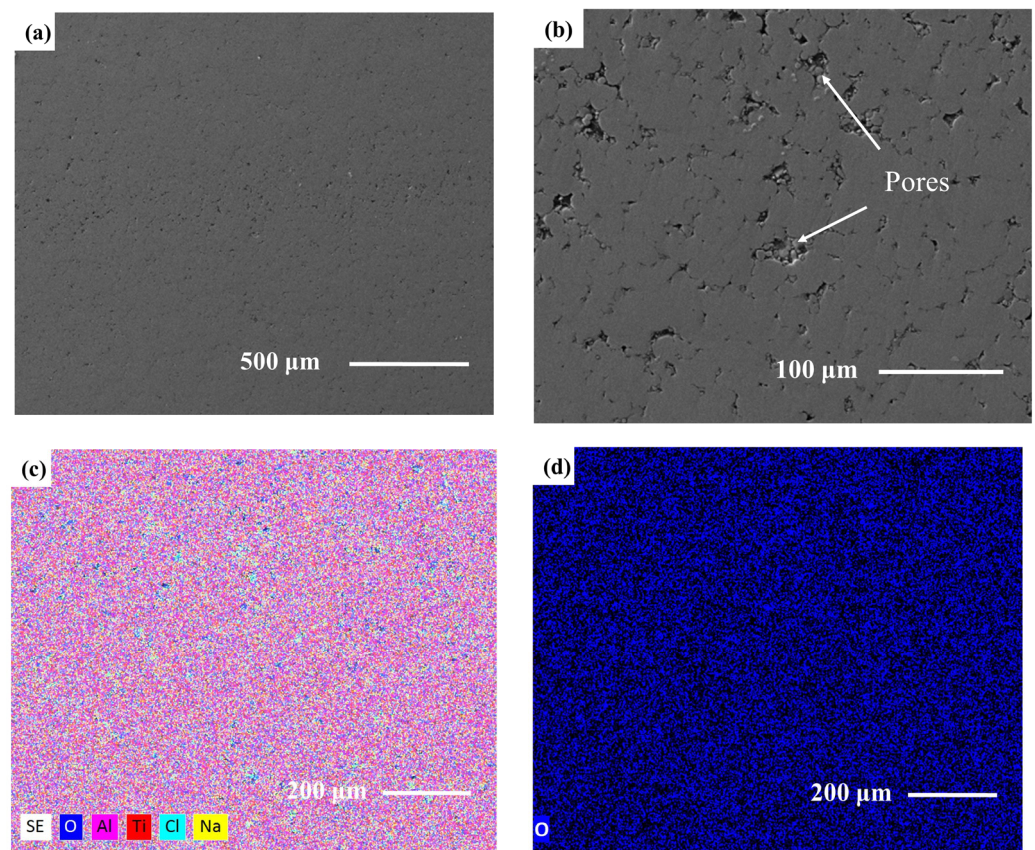


Figure 13. Morphologies of the corrosion of cold sprayed TC4 alloy coating (a,b) SEM morphologies, and (c,d) EDS analysis in Figure 13a.

4. Conclusions

(1) It is feasible to prepare a TC4 alloy coating on a Mg-Li alloy by cold spraying. The interface between the coating and the Mg-Li alloy substrate is mechanical bonding without significant defects. The porosity of the coating is approximately 4.3%.

(2) The TC4 alloy coating has higher hardness and wear resistance than the Mg-Li alloy substrate. The wear volume of the cold sprayed TC4 alloy was only 38% of that of the Mg-Li alloy. The wear mechanism of the Mg-Li alloy substrate is mainly adhesive wear, accompanied by abrasive wear and fatigue wear. Furthermore, abrasive wear was the major wear mechanism of TC4 alloy coating, accompanied by slight adhesive wear and fatigue wear. The cold sprayed TC4 coating can be conducive to extending the service life of the Mg-Li alloy substrate in practical applications, thus reducing costs.

(3) The cold sprayed TC4 alloy coating had superior corrosion resistance than the Mg-Li alloy substrate. There were considerable cracks and corrosion products on the surface of the Mg-Li alloy. However, no significant corrosion products and only small pores were observed on the TC4 alloy coating, which can effectively resist the corrosion of 3.5 wt.% NaCl solution. The cold sprayed TC4 coating is beneficial to the application of Mg-Li alloys in coastal environments, thus prolonging the service life of Mg-Li alloys.

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References

- Wen, X.; Cui, X.; Jin, G.; Jiao, Y.; Fang, Y. A novel $\text{Ni}_2\text{MnCuSnAl}_{0.1}$ multi-principal element alloy coating to enhance the wear resistance and corrosion resistance of Mg-Li alloy. *Opt. Laser Technol.* **2021**, *142*, 107243. [\[CrossRef\]](#)
- Jiang, L.; Cui, X.; Jin, G.; Tian, H.; Tian, Z.; Zhang, X.; Wan, S. Synthesis and microstructure, properties characterization of Ni-Ti-Cu/Cu-Al functionally graded coating on Mg-Li alloy by laser cladding. *Appl. Surf. Sci.* **2021**, *575*, 151645. [\[CrossRef\]](#)
- Guo, J.; Guo, S.; Shen, Y.; Li, D. Hot Deformation Behavior and Microstructural Evolution Based on the Processing Map of Dual-Phase Mg-Li Based Alloy. *Materials* **2022**, *15*, 1022. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zou, Y.; Liu, S.H.; Wang, Q.L.; Li, Y. A Comparative Study on Mechanical and Corrosion Behaviours of $\alpha/(\alpha + \beta)$ Mg-Li Al-loys Subjected to Ultrasonic Nanocrystal Surface Modification. *Metals* **2022**, *12*, 681. [\[CrossRef\]](#)
- Fathi, M.; Safavi, M.S.; Mahdavi, S.; Mirzazadeh, S.; Charkhesht, V.; Mardanifar, A.; Mehdipour, M. Co-P alloy matrix composite deposits reinforced by nano- MoS_2 solid lubricant: An alternative tribological coating to hard chromium coatings. *Tribol. Int.* **2021**, *159*, 106956. [\[CrossRef\]](#)
- Safavi, M.S.; Fathi, M.; Ahadzadeh, I. Feasible strategies for promoting the mechano-corrosion performance of Ni-Co based coatings: Which one is better? *Surf. Coat. Technol.* **2021**, *420*, 127337. [\[CrossRef\]](#)
- Miyakita, N.; Tanigaki, N.; Morishige, T.; Takenaka, T. Effect of Voltage on Mg-Li-Al Alloy Anodic Oxide Film. *Mater. Sci. Forum* **2018**, *941*, 1194–1197. [\[CrossRef\]](#)
- Lee, S.-J.; Do, L.H.T. Effects of copper additive on micro-arc oxidation coating of LZ91 magnesium-lithium alloy. *Surf. Coat. Technol.* **2016**, *307*, 781–789. [\[CrossRef\]](#)
- Zou, Y.; Zhang, Z.; Liu, S.; Chen, D.; Wang, G.; Wang, Y.; Zhang, M.; Chen, Y. Ultrasonic-Assisted Electroless Ni-P Plating on Dual Phase Mg-Li Alloy. *J. Electrochem. Soc.* **2015**, *162*, C64–C70. [\[CrossRef\]](#)
- Zhang, H.; Yao, G.; Wang, S.; Liu, Y.; Luo, H. A chrome-free conversion coating for magnesium–lithium alloy by a phosphate–permanganate solution. *Surf. Coat. Technol.* **2008**, *202*, 1825–1830. [\[CrossRef\]](#)
- Zhao, X.; Dong, T.; Fu, B.; Li, G.; Liu, Q.; Li, Y. Microstructure and Properties of Cold Sprayed NiCrAl Coating on AZ91D Magnesium Alloy. *Coatings* **2021**, *11*, 193. [\[CrossRef\]](#)
- Moridi, A.; Hassani-Gangaraj, S.M.; Guagliano, M.; Dao, M. Cold spray coating: Review of material systems and future perspectives. *Surf. Eng.* **2014**, *30*, 369–395. [\[CrossRef\]](#)
- Sun, W.; Chu, X.; Lan, H.; Huang, R.; Huang, J.; Xie, Y.; Huang, G. Current Implementation Status of Cold Spray Technology: A Short Review. *J. Therm. Spray Technol.* **2022**, *31*, 848–865. [\[CrossRef\]](#)
- Li, W.; Cao, C.; Yin, S. Solid-state cold spraying of Ti and its alloys: A literature review. *Prog. Mater. Sci.* **2020**, *110*, 100633. [\[CrossRef\]](#)
- Daroonparvar, M.; Khan, M.U.F.; Saadeh, Y.; Kay, C.M.; Kasar, A.K.; Kumar, P.; Esteves, L.; Misra, M.; Menezes, P.; Kalvala, P.R.; et al. Modification of surface hardness, wear resistance and corrosion resistance of cold spray Al coated AZ31B Mg alloy using cold spray double layered Ta/ Ti coating in 3.5 wt % NaCl solution. *Corros. Sci.* **2020**, *176*, 109029. [\[CrossRef\]](#)
- Khun, N.W.; Tan, A.W.Y.; Sun, W.; Liu, E. Wear and Corrosion Resistance of Thick Ti-6Al-4V Coating Deposited on Ti-6Al-4V Substrate via High-Pressure Cold Spray. *J. Therm. Spray Technol.* **2017**, *26*, 1393–1407. [\[CrossRef\]](#)
- Sun, W.; Tan, A.W.Y.; Marinescu, I.; Toh, W.Q.; Liu, E. Adhesion, tribological and corrosion properties of cold-sprayed CoCrMo and Ti6Al4V coatings on 6061-T651 Al alloy. *Surf. Coat. Technol.* **2017**, *326*, 291–298. [\[CrossRef\]](#)
- Singh, S.; Raman, R.K.S.; Berndt, C.C.; Singh, H. Influence of Cold Spray Parameters on Bonding Mechanisms: A Review. *Metals* **2021**, *11*, 2016. [\[CrossRef\]](#)
- Yin, S.; Cavaliere, P.; Aldwell, B.; Jenkins, R.; Liao, H.; Li, W.; Lupoi, R. Cold spray additive manufacturing and repair: Fundamentals and applications. *Addit. Manuf.* **2018**, *21*, 628–650. [\[CrossRef\]](#)
- Tiamiyu, A.A.; Schuh, C.A. Particle flattening during cold spray: Mechanistic regimes revealed by single particle impact tests. *Surf. Coat. Technol.* **2020**, *403*, 126386–126395. [\[CrossRef\]](#)
- Luo, X.-T.; Wei, Y.-K.; Wang, Y.; Li, C.-J. Microstructure and mechanical property of Ti and Ti6Al4V prepared by an in-situ shot peening assisted cold spraying. *Mater. Des.* **2015**, *85*, 527–533. [\[CrossRef\]](#)
- Fan, J.; Yun, H.; Zhang, X.; Chang, D.; Chu, X.; Xie, Y.; Huang, G. High-Performance Pure Aluminum Coatings on Stainless Steels by Cold Spray. *Coatings* **2023**, *13*, 738. [\[CrossRef\]](#)
- Wang, H.J.; Wu, S.S.; Zhang, K.J.; Sun, W.; Huang, R.Z.; Yu, M.; Xie, Y.C. Microstructure and Properties of Cold Sprayed IN718 Coating. *Surf. Technol.* **2022**, *51*, 361–369.
- Jiang, X.; Overman, N.; Smith, C.; Ross, K. Microstructure, hardness and cavitation erosion resistance of different cold spray coatings on stainless steel 316 for hydropower applications. *Mater. Today Commun.* **2020**, *25*, 101305–101314. [\[CrossRef\]](#)

25. Boruah, D.; Ahmad, B.; Lee, T.L.; Kabra, S.; Syed, A.K.; McNutt, P.; Dore, M.; Zhang, X. Evaluation of residual stresses induced by cold spraying of Ti-6Al-4V on Ti-6Al-4V substrates. *Surf. Coat. Technol.* **2019**, *374*, 591–602. [[CrossRef](#)]
26. Liu, R.; Li, D.Y. Modification of Archard's equation by taking account of elastic/pseudoelastic properties of materials. *Wear* **2001**, *251*, 956–964. [[CrossRef](#)]
27. Wang, T.; Wang, C.H.; Zhu, L.; Wang, H.; Zhang, Y. Effect of Different Substrate Angles on Wear Resistance of Laser Cladding Ni25/WC Coating. *Surf. Technol.* **2022**, *51*, 371–379.
28. Shen, M.; Zhu, X.; Han, B.; Ying, T.; Jia, J. Dry sliding wear behaviour of AZ31 magnesium alloy strengthened by nanoscale SiCp. *J. Mater. Res. Technol.* **2022**, *16*, 814–823. [[CrossRef](#)]
29. Koricherla, M.; Torgerson, T.; Alidokht, S.; Munagala, V.; Chromik, R.; Scharf, T. High temperature sliding wear behavior and mechanisms of cold-sprayed Ti and Ti-TiC composite coatings. *Wear* **2021**, *476*, 203746. [[CrossRef](#)]
30. Yang, L.H.; Lin, C.G.; Gao, H.P.; Xu, W.C.; Li, Y.T.; Hou, B.R.; Huang, Y.L. Corrosion Behaviour of AZ63 Magnesium Alloy in Natural Seawater and 3.5 wt. % NaCl Aqueous Solution. *Int. J. Electrochem. Sci.* **2018**, *18*, 8084–8093. [[CrossRef](#)]
31. Wang, Z.; Fu, B.G.; Wang, Y.F.; Dong, T.S.; Li, J.K.; Li, G.L.; Zhao, X.B.; Liu, J.H.; Zhang, G.X. Effect of Cu Content on the Precipitation Behaviors, Mechanical and Corrosion Properties of As-Cast Ti-Cu Alloys. *Materials* **2022**, *15*, 1696. [[CrossRef](#)] [[PubMed](#)]
32. Acquesta, A.; Sinagra, C.; Monetta, T. Electrochemical and Economic Analysis of No-Rinse, “True-Cr-Free” Surface Conversion Coatings for a Green, Cost-Saving, Corrosion Protection of 8079 Aluminium Alloy. *Appl. Sci.* **2023**, *13*, 1560. [[CrossRef](#)]
33. Xie, C.; Li, H.; Zhou, X.; Sun, C. Corrosion behavior of cold sprayed pure zinc coating on magnesium. *Surf. Coat. Technol.* **2019**, *374*, 797–806. [[CrossRef](#)]
34. Li, R.; Fu, B.; Wang, Y.; Li, J.; Dong, T.; Li, G.; Zhang, G.; Liu, J. Effect of Cold-Rolling Reduction on Recrystallization Microstructure, Texture and Corrosion Properties of the X2CrNi12 Ferritic Stainless Steel. *Materials* **2022**, *15*, 6914. [[CrossRef](#)] [[PubMed](#)]
35. Bijalwan, P.; Singh, C.; Kumar, A.; Sarkar, K.; Rani, N.; Laha, T.; Banerjee, A.; Mondal, K. Corrosion behaviour of plasma sprayed Fe based metallic glass (Fe₇₃Cr₂Si₁₁B₁₁C₃ (at%)) coatings in 3.5% NaCl solution. *J. Non-Cryst. Solids* **2021**, *567*, 120913–120925. [[CrossRef](#)]

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