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Article

Corrosion Resistance of TiB₂ Coatings in Molten Zinc Fabricated by Electrophoretic Deposition in Molten Salts

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Abstract: To enhance the corrosion resistance of molybdenum metal in molten zinc, this study successfully fabricated TiB₂ coatings on molybdenum substrates using the molten salt electrophoretic deposition technique and investigated their corrosion resistance in molten zinc. Initially, TiB₂ nanoparticles with a size ranging from 50 to 150 nm were synthesized using the borothermal reduction method in NaF-AlF₃ molten salts at 1238 K. Subsequently, electrophoretic deposition experiment was conducted by applying a cell voltage of 1.2 V (corresponding to an electric field of 0.6V/cm) for 1 h in the molten salts containing TiB₂ nanoparticles, resulting in a uniform, continuous, and dense TiB₂ coating with a thickness of 35 μm on the molybdenum substrate. Moreover, the corrosion resistance of the TiB₂ coated molybdenum metal to molten zinc was tested through continuous immersion. After 120 h of immersion, the TiB₂ coating showed no signs of cracking or peeling off, successfully protecting the molybdenum metal substrate from corrosion by molten zinc. The results confirm that the molten salt electrophoretic deposition technique can be used to prepare TiB₂ coatings with good resistance to molten zinc corrosion on molybdenum metal.

Keywords: molten salt; electrophoretic deposition; molybdenum metal; TiB₂ coating; corrosion resistance in molten zinc

1. Introduction

Molybdenum and its alloys are extensively utilized in zinc alloy casting and the hot-dip galvanizing of steel, owing to their high melting points and corrosion resistance [1–3]. In order to enhance the corrosion resistance of molybdenum and its alloys in molten zinc, researchers have explored two aspects: optimizing the microstructure of molybdenum metal [3,4] and enhancing its surface characteristics [5–7]. Although adjustments to the composition and structure of molybdenum metal can effectively enhance its corrosion resistance to molten zinc, this strategy also inevitably leads to increased complexity in material processing and higher costs [9,10]. Therefore, enhancing the corrosion resistance of molybdenum metals to molten zinc through the surface treatment technique is a more effective and cost-efficient approach.

Transition metal borides, due to their high melting points, excellent thermal conductivity, and chemical stability at elevated temperatures, are ideal surface coating materials for resisting corrosion by molten zinc [11–14]. To date, researchers have investigated the corrosion resistance of transition metal boride coatings such as ZrB₂ [15], TiB₂-Al₂O₃ [16], MoB-CoCr [17], and FeB/FeB₂ [18] in molten zinc, achieving satisfactory results. The primary methods currently used for fabricating transition metal boride coatings resistant to molten zinc corrosion include molten salt electrodeposition [19], plasma spraying [20], supersonic flame spraying [21], and boron infiltration treatment [22]. However, these methods are still limited by the complexity of the process, high equipment costs, and poor

coating quality, necessitating further optimization or the development of entirely new coating manufacturing technologies.

In recent years, authors of this paper have successfully developed a novel method for the fabrication of transition metal boride coatings such as TiB_2 and ZrB_2 : molten salt electrophoretic deposition (MS-EPD) [23–26]. This method offers several significant advantages: it features a streamlined process, does not rely on expensive equipment, and yields coatings with dense and high-purity characteristics. This study synthesized nanoscale TiB_2 particles via the borothermal reduction of titanium dioxide in NaF-AlF_3 molten salts. Subsequently, by applying cell voltages to the NaF-AlF_3 molten salts containing TiB_2 nanoparticles (NPs), a dense TiB_2 coating was formed on the cathodic molybdenum metal substrate via the electrophoretic deposition (EPD) process. This paper tested the corrosion resistance of TiB_2 coated molybdenum metal substrates against molten zinc. The results indicated that TiB_2 coatings, prepared via the EPD technique, can effectively protect the molybdenum substrate from molten zinc corrosion, potentially enhancing the performance of molybdenum and its alloys in extreme environments.

2. Materials and experimental procedure

2.1. EPD of TiB_2 coatings in NaF-AlF_3 molten salts

The process of preparing TiB_2 coatings by MS-EPD consists of two steps. First, nano- TiB_2 were synthesized via borothermal reduction in NaF-AlF_3 molten salts. Subsequently, EPD was conducted in the same molten salts containing nano- TiB_2 to prepare TiB_2 coatings, as illustrated in Figure 1.

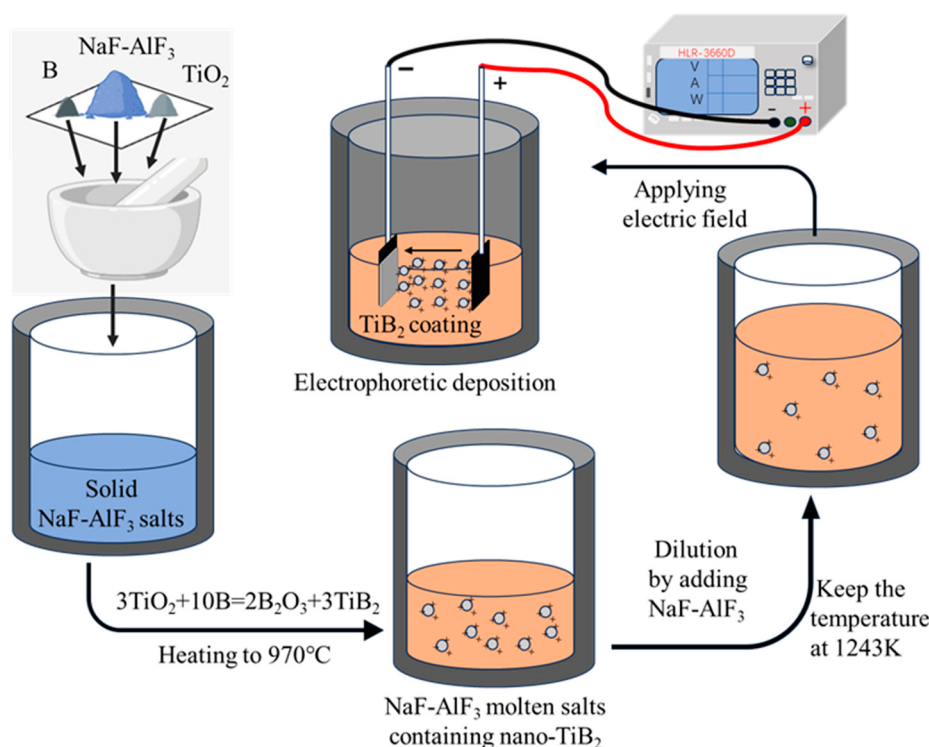


Figure 1. Schematic of the process for the synthesis of nano- TiB_2 in molten salts and the preparation of TiB_2 coatings by EPD.

(1) Synthesis of nano- TiB_2 via borothermal reduction in molten salts

As shown in Figure 1, the mixture consisted of NaF , AlF_3 , TiO_2 and B was ground in an agate mortar for 15 min. The well ground mixture was added to a graphite crucible which was placed in a sealed resistance furnace. Afterwards, the furnace was heated from room temperature to 1238 K through 100 min and then held for 3 h to fully react and synthesize the TiB_2 NPs. Subsequently, 75 g

NaF-AlF₃ solid mixture were added to the TiB₂ NPs-contained molten salts to dilute them. After waiting for 1 h, the molten salts were ready for the EPD experiment.

(2) EPD of TiB₂ coatings

Subsequently, a molybdenum cathode (4 × 2 × 25 mm) was immersed to a depth of 15 mm below the surface of the prepared TiB₂-contained molten salts and a graphite anode (6 × 3 × 50 mm) was immersed to a depth of 15-20 mm. The distance between anode and cathode was 15 mm, as shown in Figure 1. A DC power supply (HLR-3660D, Henghui) was used to control the cell voltages. The experimental temperature was 1238 K and the duration of EPD was 60 min. Upon completion of the MSS-EPD experiment, the cathode was removed and cleaned by soaking in deionized water for 1 h before characterized. All EPD experiments were conducted under an argon atmosphere.

2.2. Corrosion resistance test of TiB₂ coatings in molten zinc

This study utilized high-purity (≥99.99%) zinc, provided by Beijing Jinyuan New Material Technology Co., Ltd., as the corrosive medium to assess the corrosion resistance of TiB₂ coatings in molten zinc. Zinc plates were initially cut into 30 × 20 × 5 mm³ dimensions and finely ground using 1000-grit sandpaper. After grinding, the samples were ultrasonically cleaned with acetone and alcohol to remove surface impurities and then air-dried at room temperature. The pretreated zinc blocks were heated in an alumina crucible in a high-temperature furnace until fully melted, ensuring complete material fusion. TiB₂ coated molybdenum metal samples were initially held above the molten zinc surface for 30 s and then slowly immersed into the melt to prevent coating cracking or detachment due to thermal stress. Static corrosion tests were conducted on both TiB₂ coated samples and uncoated molybdenum at a temperature of 823 K. The exposure times for TiB₂ coated samples in molten zinc were set at 12, 24, 48, 96, and 120 h, while uncoated molybdenum substrates were exposed for 2 and 4 h, respectively. Following the corrosion tests, the samples were removed from the molten zinc, cooled at room temperature, and the solidified zinc adhering to the sample surfaces was preserved for subsequent observation and analysis.

2.3. Characterization

The synthesized TiB₂ NPs and cross-sectional morphologies of TiB₂ coatings were characterized with a scanning electron microscopy (SEM, model: Tescan Mira3) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (brand: Oxford Instruments). Furthermore, X-ray diffraction (XRD) (Rigaku Ultima IV, operating voltage: 40 kV, current: 40 mA, scanning speed: 10°/min) was employed to analyze the crystallographic phase composition of TiB₂ NPs and TiB₂ coatings. The adhesion strength of the coating to substrate was evaluated using a Revetest Scratch Tester, an automatic device for assessing thin film adhesion, produced by CSM Instruments in Switzerland. This device can apply a linear load up to 100 N, with a loading rate of 19.8 N/min and a scratch speed of 1 mm/min, while maintaining a scratch length at 5 mm. Samples subjected to corrosion testing in molten zinc were analyzed using SEM equipped with an EDS detector to assess their surface morphology and elemental composition.

3. Results and discussion

3.1. Synthesis of TiB₂ NPs and EPD of TiB₂ coatings in NaF-AlF₃ molten salts

After the borothermal reduction of titanium dioxide experiment, the molten salts contain TiB₂ NPs were recovered when they were naturally cooled down to room temperature. The solidified salts were characterized using XRD and SEM, the results were presented in Figure 2.

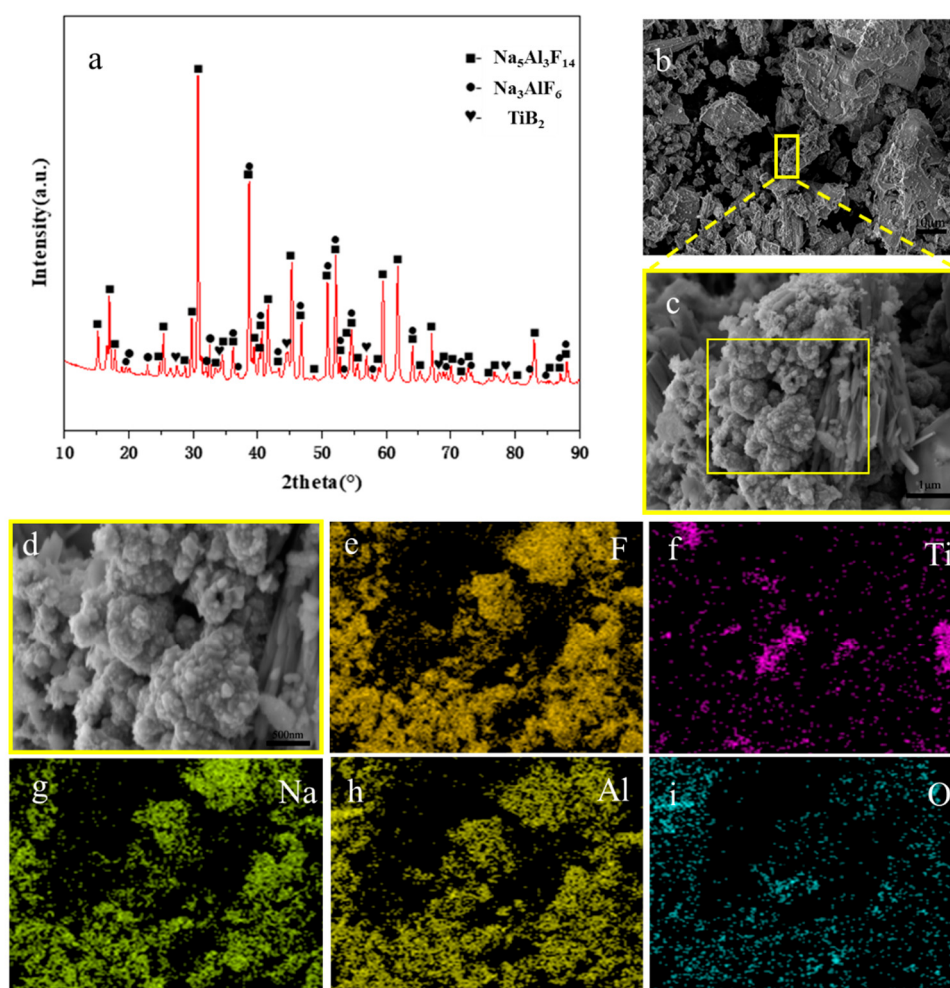


Figure 2. XRD result (a) and SEM images (b-d) of recovered solid salts containing TiB_2 NPs. Elemental EDS mapping analysis for F, Ti, Na, Al and O (e-i) corresponding to (b).

XRD analysis of the NaF-AlF_3 solid salt containing TiB_2 (Figure 2a) indicated that the salt was primarily composed of three substances: TiB_2 , Na_3AlF_6 , and $\text{Na}_5\text{Al}_3\text{F}_{14}$. Morphologies of the sample reveals that the solid salts were consisted of nanoscale particles (Figure 2b-d). Elemental EDS mapping analysis demonstrates the distribution of F, Ti, Na, Al, and O (Figure 2e-i) within the sample. The enrichment of Ti element was observed, distributed in salts containing Na, Al and F elements and the distribution characteristics of Ti and O indicated those regions enriched with titanium have lower oxygen content. Further magnified SEM characterization of the location enriched with Ti (yellow rectangular area in Figure 2 b) revealed existence of numerous dispersed particles from 50 to 150 nm, as seen in Figure 2 c. In conjunction with the XRD results, nanoscale TiB_2 particles were successfully synthesized through the borothermal reduction reaction.

Following the successful synthesized TiB_2 NPs via borothermal reduction in NaF-AlF_3 molten salts, the EPD experiment was conducted by applying a cell voltage of 1.2 V for 1 h, resulting in a TiB_2 coating on the molybdenum cathode. Figure 3(a) showed the XRD result of the EPDed TiB_2 coating on the molybdenum substrate. The result indicated that no other substances existed besides TiB_2 and Mo. It confirmed the acquisition of a relatively pure TiB_2 coating through the MS-EPD technique. Figure 3(b) showed a cross-sectional low magnification image of the TiB_2 coating along with the corresponding elemental spectra. The thickness of the TiB_2 coating was approximately 35 μm and the coating was dense, continuous and uniform, with a smooth surface and no apparent defects. Figure 3(c) and Figure 3(d) showed further magnification and line scan analysis of the area shown in Figure 3(b). High magnification SEM image indicated that the TiB_2 coating prepared by MS-

EPD was fully dense, The results of EDS line scans of Ti and Mo elements revealed absence of obvious compositional transition layer at the interface between the TiB_2 coating and the molybdenum substrate.

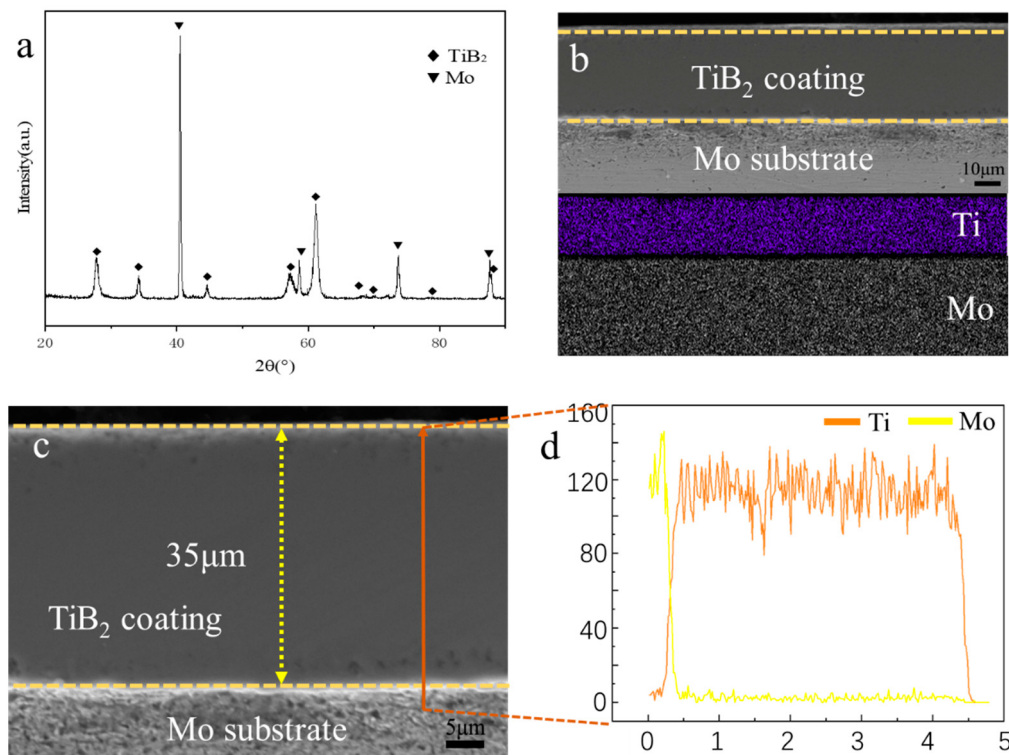


Figure 3. (a) XRD analysis of the TiB_2 coated molybdenum metal. (b) Cross-sectional low magnification SEM image with corresponding elemental mapping for Ti and Mo. (c,d) Cross-sectional high magnification SEM image with line scan analysis.

The adhesion strength between the TiB_2 coating and the molybdenum substrate was assessed using a scratch test, with results depicted in Figure 4. A linear load from 0 to 100 N was progressively applied over a 5 mm scratch length. A slight fluctuation in the acoustic signal was observed when the load increased to 37 N. At a load of 44 N, a strong vibration in the acoustic signal occurred, coinciding with the initiation of coating delamination, thereby determining the critical adhesion strength (L_{c3}) between the TiB_2 coating and the molybdenum substrate as 44 N. It confirmed that the TiB_2 coating fabricated by MS-EPD exhibited robust adhesion to the molybdenum metal substrate.

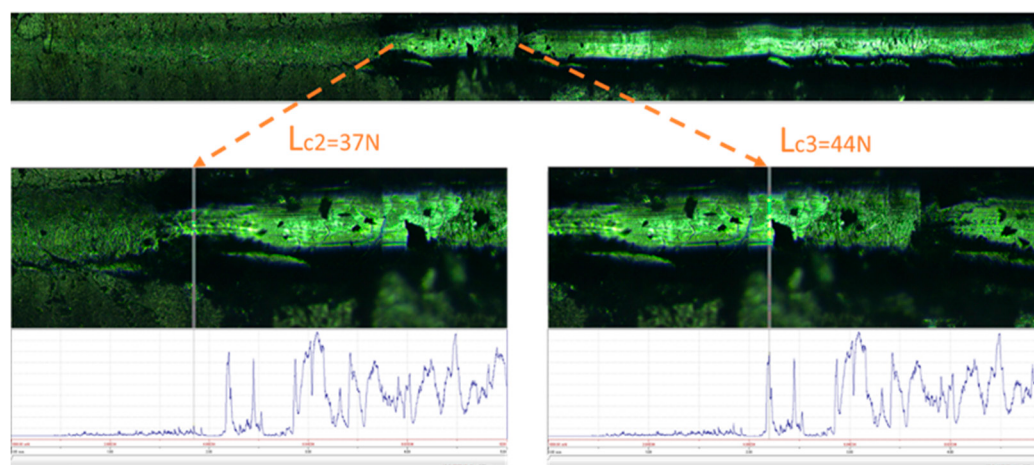


Figure 4. Scratch test for the adhesion strength of the TiB_2 coating on the molybdenum substrate.

3.2. Corrosion behavior of uncoated molybdenum in molten zinc

Utilizing the MS-EPD technique, a TiB_2 coating with high adhesion strength and dense structure was successfully fabricated on a molybdenum substrate. Before examining the corrosion resistance properties of the TiB_2 coating in molten zinc, this study conducted a systematic investigation into the corrosion behavior of molybdenum metal in molten zinc at 823 K, with soaking durations of 2 and 4 h. After the experiment, detailed testing and analysis were conducted on the molybdenum samples, with results presented in Figure 5 and Figure 6.

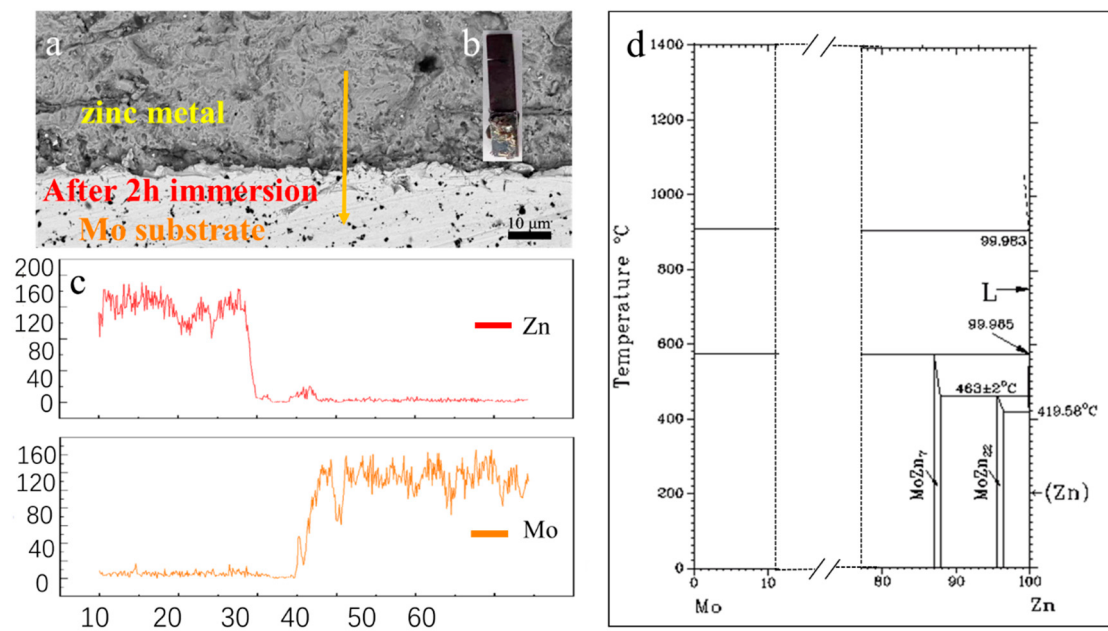


Figure 5. Corrosion resistance results of uncoated molybdenum in molten zinc (2 h). (a) Cross-sectional SEM image of molybdenum. (b) Appearance of molybdenum after immersion in molten zinc. (c) Line scan image at the interface between molybdenum and solid zinc. (d) Molybdenum-zinc binary phase diagram.

After immersion in molten zinc at 823 K for 2 h and subsequent cooling, the molybdenum metal exhibited a surface covered with a layer of solid zinc, demonstrating good wettability, as shown in Figure 5b. Analysis of the zinc-coated molybdenum cross-section using SEM (Figure 5a) revealed a transition layer approximately 8 μm thick between the molybdenum metal and the surface zinc. EDS line scan analysis (Figure 5c) disclosed the coexistence of molybdenum and zinc elements within the transition layer, indicating erosion of the molybdenum metal by the molten zinc. According to the molybdenum-zinc binary phase diagram (Figure 5d), at 823 K, various intermetallic compounds such as MoZn_3 and MoZn_7 could potentially form, depending on the concentrations of molybdenum and zinc. This finding confirms that a chemical reaction occurred between the molybdenum metal and molten zinc, illustrating the inability of molybdenum to resist the corrosive effects of molten zinc.

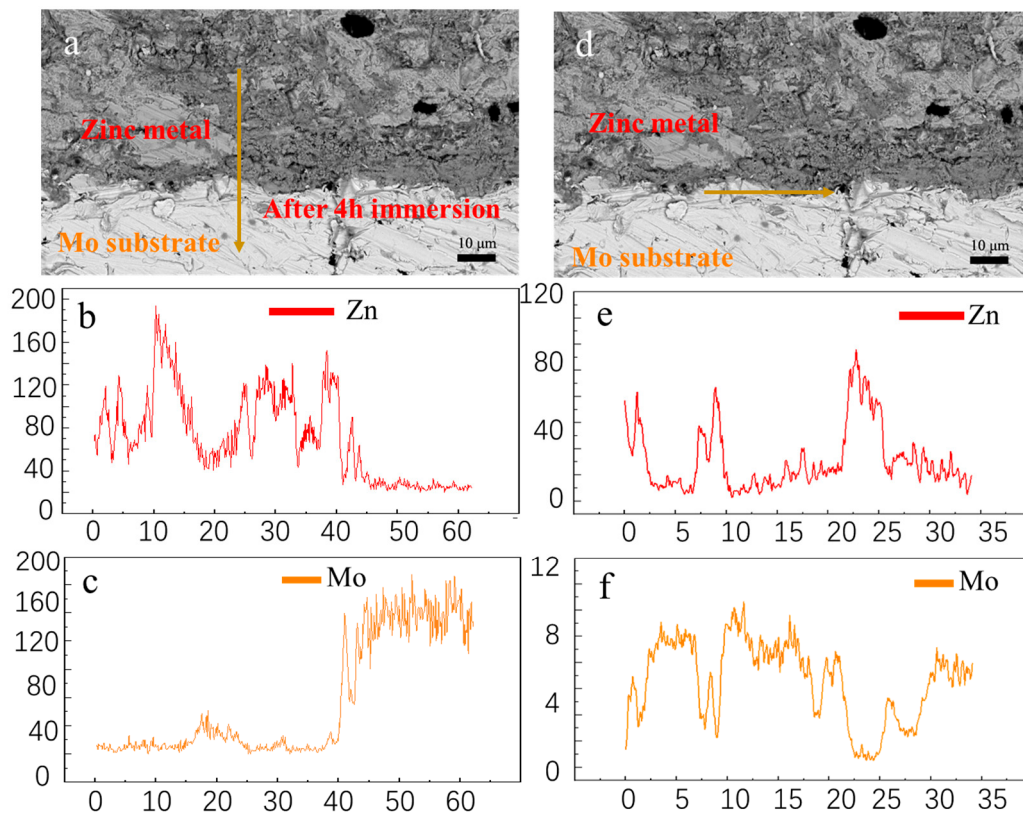


Figure 6. Corrosion resistance results of uncoated molybdenum in molten zinc (4 h). (a) and (d) are cross-sectional SEM images of the molybdenum metal. (b) and (c) are the longitudinal line scan analyses of the interface between the molybdenum metal and solid zinc. (e) and (f) are the transverse line scan analyses of the interface between the molybdenum metal and solid zinc.

Given that the cross-sectional images of molybdenum after a 2 h immersion in molten zinc did not clearly reveal the corroded layer, this study extended the immersion to 4 h, with results presented in Figure 6. A transition layer approximately 28 μm thick formed at the interface between the molybdenum and solid zinc, as shown in Figure 6a and Figure 6d. Longitudinal EDS linear scan analysis indicated the coexistence of molybdenum and zinc elements within the transition layer, as depicted in Figure 6b and Figure 6c, revealing that the degree of molybdenum corrosion significantly increased with the extension of immersion time from 2 to 4 h. Transverse EDS linear scans, as shown in Figure 6e and Figure 6f, revealed fluctuations in the concentration of zinc and molybdenum elements at the interface, likely due to the unevenness of the molybdenum surface and varying diffusion rates between molybdenum and zinc. In summary, since molybdenum forms intermetallic compounds with zinc at 823 K and exhibits relatively weak resistance to corrosion by molten zinc, the use of protective coatings is particularly important.

3.3. Corrosion behavior of molybdenum with TiB₂ coatings in molten zinc

The MS-EPD technique was successfully utilized to form a fully dense TiB₂ coating on the molybdenum surface. To thoroughly evaluate the resistance of TiB₂ coatings to corrosion in molten zinc, a series of corrosion experiments with varying immersion durations (12, 24, 48, 96, and 120 h) were designed and conducted. Figure 7 presents the corrosion test results for the TiB₂ coated samples with immersion times of 12, 24, and 48 h, respectively.

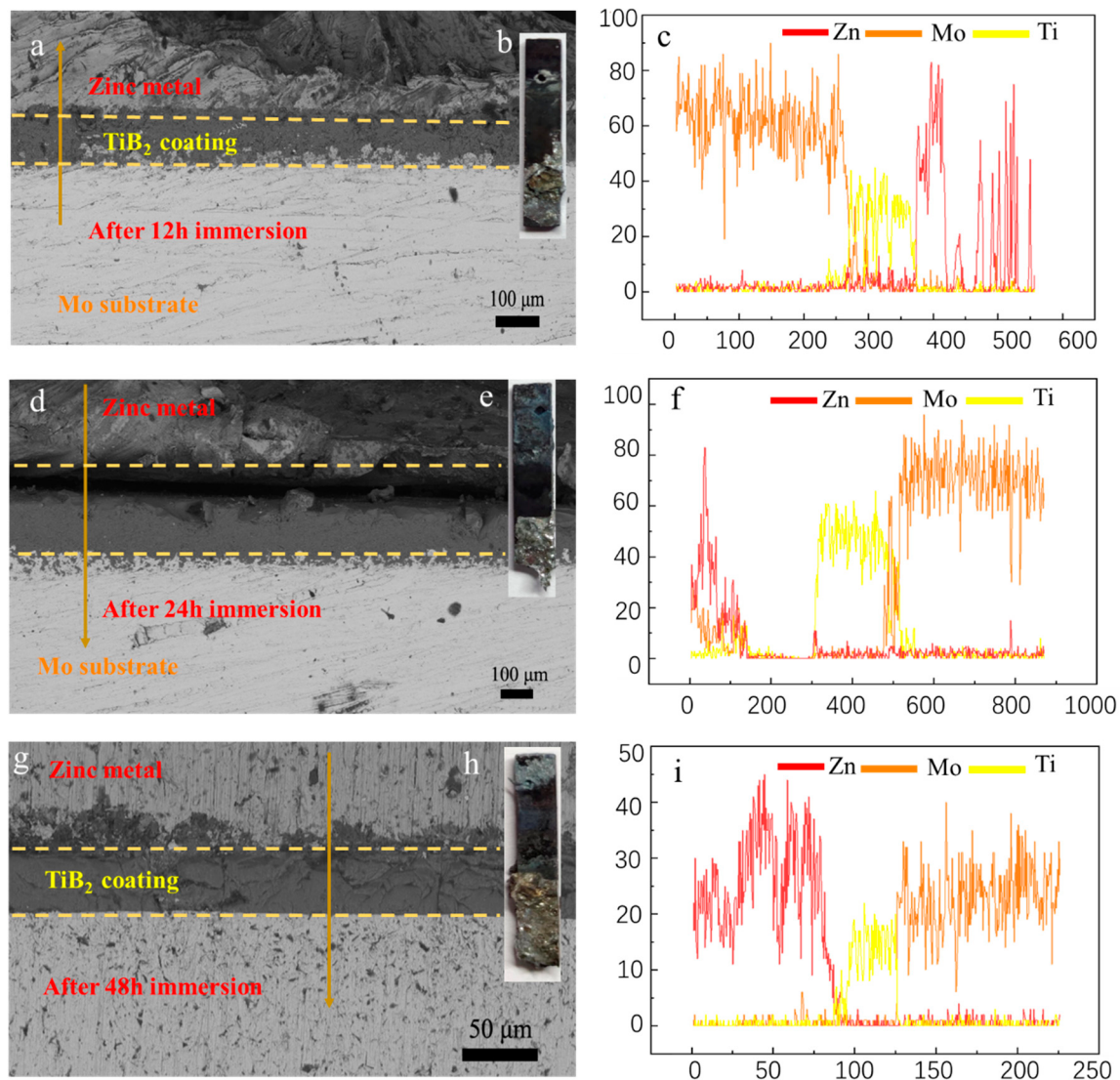


Figure 7. Cross-sectional morphologies and EDS linear scan analysis results of molybdenum with TiB₂ coatings after immersion in molten zinc for various durations: 12 h (a, b, c); 24 h (d, e, f); 48 h (g, h, i).

The appearance images of the TiB₂ coating after immersion in molten zinc for 12, 24, and 48 h (Figure 7b, e, h) show that the surface is uniformly encapsulated by solid zinc, indicating good wettability between the TiB₂ coating and the molten zinc. Cross-sectional SEM images (Figure 7a, d, g) and corresponding line scan analyses (Figure 7c, f, i) reveal that the TiB₂ coating, after immersion for 12, 24, and 48 h in molten zinc, remains intact without corrosion damage, exhibits no cracks, and maintains strong adhesion to the molybdenum substrate. No new substances were observed at the interface between zinc and the TiB₂ coating; only physical adhesion was evident. This suggests that within 48 h, no chemical reaction occurred between the TiB₂ coating and the molten zinc, effectively protecting the molybdenum substrate from corrosion.

In this study, the immersion time of the TiB₂ coating in molten zinc was extended to 96 h to assess its long-term corrosion resistance. Figure 8(a) presents the cross-sectional morphology of the TiB₂ coating after 96 h of immersion, revealing an intact, dense, and continuous structure indicative of excellent corrosion resistance. A magnified view of the coating's corner area (Figure 8b) further confirms that the TiB₂ coating effectively protected the molybdenum substrate against long-term erosion by molten zinc, showing no significant signs of corrosion or damage. Linear scan analysis across the cross-section (Figure 8d-f) shows a dramatic reduction in zinc content near the interface between the TiB₂ coating and the zinc, approaching zero. This finding suggests that over the 96 h

immersion period, zinc did not significantly infiltrate the TiB_2 coating through chemical reactions or diffusion, thereby validating the protective efficacy of the TiB_2 coating on the molybdenum substrate.

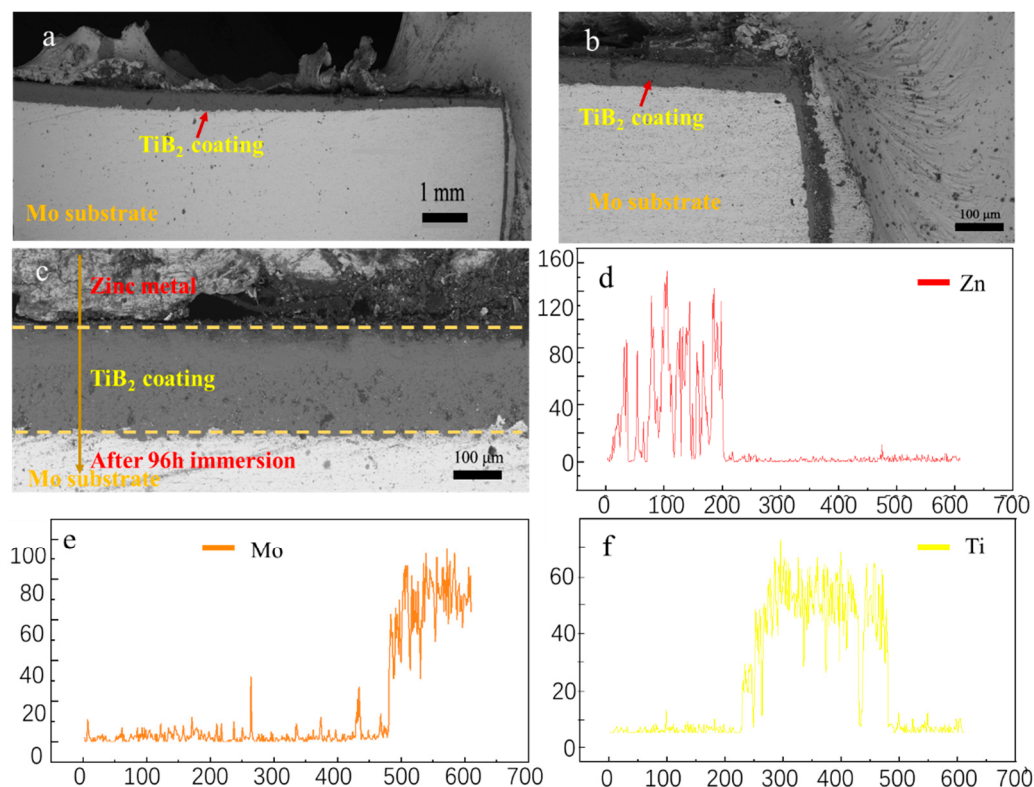


Figure 8. Corrosion resistance results of molybdenum with TiB_2 coatings in molten zinc (96h). (a) Low magnification cross-sectional SEM image. (b) High magnification SEM image at the corner. (c) High magnification SEM image on the flat surface. (d-f) Line scan analysis results.

This study extended the immersion time of the TiB_2 coating in molten zinc to 120 h to further investigate its corrosion resistance. Figure 9a-c display the morphologies of the TiB_2 coating cross-section after 120 h of exposure to molten zinc. The results show that despite prolonged exposure to a corrosive environment, the TiB_2 coating remained crack-free and fully dense. Longitudinal linear scan results (Figure 9d-f) reveal that at the interface between the TiB_2 coating and solid zinc, zinc concentration sharply decreases to zero, without any overlapping distribution of titanium elements. This finding confirms that no significant chemical reactions or elemental diffusion occurred between the TiB_2 coating and molten zinc. Elemental mapping analysis of the TiB_2 coating cross-section, as shown in Figure 8c, indicates no apparent mixing of molybdenum (Mo), titanium (Ti), and zinc (Zn) at the interface. In summary, after 120 h of immersion in molten zinc, zinc elements failed to penetrate the interior of the TiB_2 coating through chemical reactions or diffusion. It can be concluded that the TiB_2 coating, prepared via MS-EPD, effectively protects the molybdenum substrate from corrosion by molten zinc.

The TiB_2 coating on the molybdenum substrate exhibits excellent resistance to liquid zinc corrosion, primarily due to four factors: Experimental results indicate that no chemical reaction occurs between liquid zinc and TiB_2 at 823 K, resulting in no new substances being formed. Notably, the solubility of TiB_2 in liquid zinc at 823 K is relatively low, contributing to the coating's stability and corrosion resistance. The NaF-AlF_3 molten salts effectively dissolves TiO_2 and B_2O_3 [27], enabling the preparation of a low-oxygen TiB_2 coating via MS-EPD. This low-oxygen coating prevents intergranular corrosion, thereby enhancing its corrosion resistance. A solid solution reaction between molybdenum and TiB_2 [28] forms a metallurgical bond. Additionally, the thermal expansion coefficients of molybdenum and TiB_2 are closely matched, at $4.8 \times 10^{-6} \text{ K}^{-1}$ [29] and $5.5 \times 10^{-6} \text{ K}^{-1}$ [30], respectively. These closely matched thermal expansion coefficients and high bonding strength ensure

that the coating remains intact during temperature fluctuations. In summary, the TiB_2 coating prepared on the molybdenum substrate using MS-EPD technology exhibits remarkable resistance to liquid zinc corrosion. This coating effectively shields the substrate from liquid zinc corrosion, offering robust protection for molybdenum in zinc-rich environments.

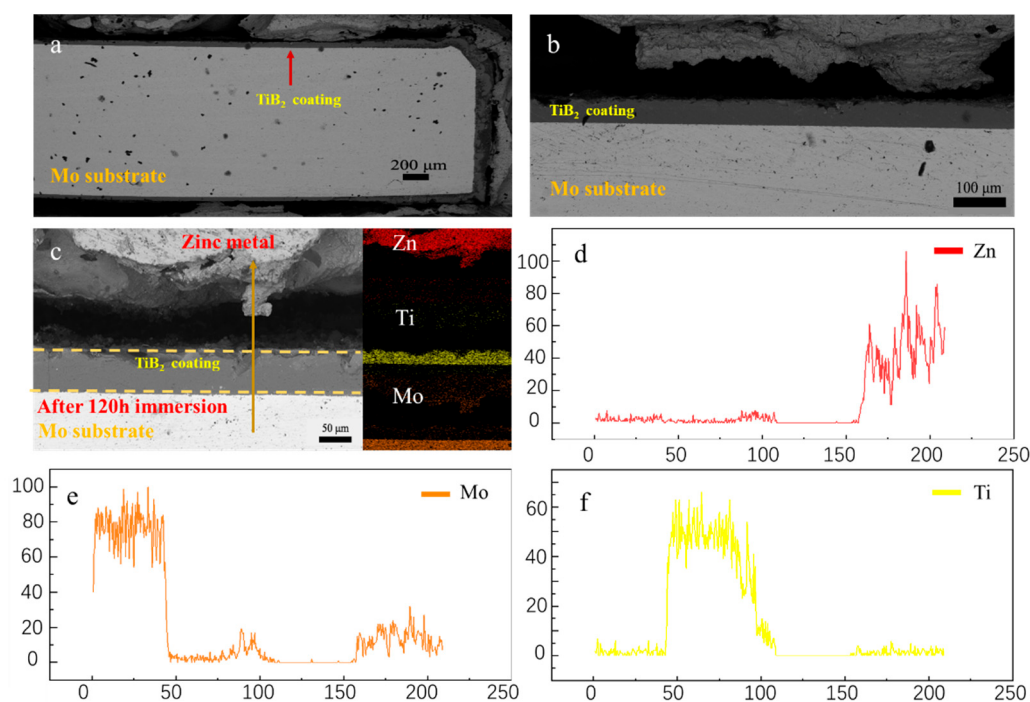


Figure 9. Corrosion resistance results of molybdenum with the TiB_2 coating. (a) in molten zinc (120h). Low magnification cross-sectional SEM image. (b) High magnification cross-sectional SEM image. (c) Cross-sectional mapping image. (d-f) Line scan analysis images.

4. Conclusion

To enhance the corrosion resistance of molybdenum in molten zinc, this study successfully fabricated TiB_2 coatings on molybdenum substrates using MS-EPD technology and thoroughly investigated the corrosion resistance of TiB_2 coatings.

1. In the NaF-AlF_3 molten salt system at 1238 K, TiB_2 particles ranging from 50 to 150 nm were synthesized through the borothermal reduction method. Under a 1.2V cell voltage, TiB_2 NPs migrated within the molten salts and deposited on the molybdenum substrate, forming a dense TiB_2 coating with high adhesion strength ($L_c=44$ N).

2. At 823 K, molybdenum reacts with molten zinc to form intermetallic compounds, rendering it unable to resist corrosion. However, the absence of a chemical reaction between TiB_2 and molten zinc at 823 K, along with the coating's dense structure and low oxygen content, enables the TiB_2 coating to exhibit excellent corrosion resistance after 120 h of immersion, effectively protecting the molybdenum substrate.

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Conflicts of Interest: The authors declare no conflict of interest.

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