

Article

Electrophoretically Deposited TiB₂ Coatings in NaF-AlF₃ Melt for Corrosion Resistance in Liquid Zinc

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Abstract: Molten salt electrophoretic deposition is a novel method for preparing coatings of transition metal borides such as TiB₂, which has emerged in recent years. To broaden the applications of transition metal boride coatings prepared by this method, this paper investigates the corrosion resistance of TiB₂ coatings, produced through molten salt electrophoretic deposition, to liquid zinc. By applying a cell voltage of 1.2 V (corresponding to an electric field of 0.6 V/cm) for 1 h in molten NaF-AlF₃, the nanoscale TiB₂ particles migrated to the cathode and were deposited on the graphite substrate, forming a smooth and dense TiB₂ coating with a thickness of 43 μm. Subsequently, after subjecting the TiB₂-coated graphite to corrosion resistance tested in molten zinc for 120 h of continuous immersion, no cracks were observed on the surface or within the coating. The produced TiB₂ coating demonstrated excellent corrosion resistance. These research results suggest that the fully dense TiB₂ coating on the graphite substrate, produced through molten salt electrophoretic deposition, exhibits excellent corrosion resistance to liquid zinc.

Keywords: electrophoretic deposition; NaF-AlF₃ molten salts; nano-TiB₂; TiB₂ coating; corrosion resistance in molten zinc



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1. Introduction

Transition metal diborides have attracted significant interest over the past several decades due to their unique attributes, including high melting points, high thermal conductivity, excellent chemical stability, and exceptional mechanical properties [1–3]. Among these materials, titanium diboride (TiB₂) has attracted significant attention [4–6]. It is worth noting that TiB₂ coatings are highly effective as protective coatings against liquid metal corrosion. This has been particularly evident in its use with aluminum [7–10] and in liquid lead-free solder alloys [11,12], where its protective properties are employed.

The primary preparation methods for TiB₂ coatings include physical vapor deposition (PVD) [13,14], chemical vapor deposition (CVD) [15], molten salt electrodeposition [16], and plasma spraying [17]. However, these methods for fabricating TiB₂ coatings exhibit shortcomings that necessitate further improvement [18]. Recently, the present authors demonstrated the feasibility of electrophoretic deposition (EPD) in molten inorganic salts [19,20] and have subsequently proposed a method for the preparation of transition metal boride coatings, such as TiB₂, through EPD in molten salts (i.e., the MS-EPD process) [21–24]. Compared to conventional coating preparation methods, this method does not require expensive equipment or complex procedures, providing an environmentally friendly and high-purity product preparation process. In order to expand the application scope of the MS-EPD (i.e., molten salt electrophoretic deposition) method for fabricating TiB₂ coatings, this study aims to investigate the corrosion resistance of TiB₂ coatings prepared through the MS-EPD method against liquid zinc corrosion, since industrial production processes

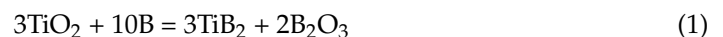
involving zinc alloy casting and hot-dip galvanizing of steel demand anti-resistant coatings for liquid zinc.

This study specifically selected graphite as the substrate material to facilitate direct observation of the microstructure of TiB₂ coating cross-sections. The main research contents include (1) successful synthesis of nanoscale TiB₂ in NaF-AlF₃ molten salts using the borothermal reduction method, which provides a prerequisite for electrophoretic deposition; (2) fabrication of a fully dense TiB₂ coating on the surface of the graphite substrate through the MS-EPD process; and (3) systematic evaluation of the corrosion resistance of the TiB₂ coating against liquid zinc.

2. Materials and Experimental Procedure

1. Synthesis of nanoscale TiB₂ via borothermal reduction in NaF-AlF₃ molten salts

The solid salts of NaF (>99%, Aladdin, Shanghai, China) and AlF₃ (analytical purity, Tianjin Guangfu, Tianjin, China) were mixed at a molar ratio of 61:39. The B powder (99%, mean size: 400 nm, Casting and Research Metal Material Co., Ltd. Qian'an, China) and TiO₂ powder (99.9%, mean size: 20 nm, Shanghai ChaoWei Nanotechnology Co., Ltd., Shanghai, China) were blended with a 15 wt% excess of B powder based on the stoichiometric ratio of Reaction 1. The NaF-AlF₃ solid salts and the mixture of B and TiO₂ powders were then blended at a 10:1 mass ratio. The mixture, comprising NaF, AlF₃, TiO₂, and B powder, was thoroughly ground in an agate mortar for 15 min to ensure homogeneity. The well-ground mixture was then transferred to a graphite crucible, which was placed in a sealed resistance furnace. The temperature was gradually increased from ambient to 1238 K over a period of 100 min, followed by a holding period of 3 h, to ensure the complete reaction and synthesis of the TiB₂ nanoparticles (NPs). Subsequently, 75 g of NaF-AlF₃ solid mixture was added to the molten salts containing the synthesized TiB₂ NPs to dilute them. After waiting for 1 h, the TiB₂ NP-containing molten salts were prepared for the EPD experiment.



2. EPD of TiB₂ coatings in NaF-AlF₃ molten salts

A graphite cathode (4 mm × 2 mm × 25 mm) was immersed to a depth of 15 mm in the prepared molten salts, while a graphite anode (6 mm × 3 mm × 50 mm) was immersed to a depth of 15–20 mm. The distance between the cathode and anode was maintained at 15 mm. A DC power supply (HLR-3660D, Henghui, Zibo, China) was utilized to control the cell voltage at 1.2 V. The EPD process was conducted at an experimental temperature of 1238 K for a duration of 60 min. After the EPD experiment, the cathode was removed and cleaned by soaking it in deionized water at room temperature for 1 h. Then, the coated specimen was subjected to physical–chemical characterization. All EPD experiments were conducted under an argon atmosphere to prevent oxidation.

3. Corrosion resistance test of the TiB₂ coating in molten zinc

This study employed high-purity (≥99.99%) zinc, sourced from Beijing Jinyuan New Material Technology Co., Ltd. (Beijing, China), as the corrosive medium to evaluate the corrosion resistance of TiB₂ coatings in molten zinc. Zinc plates were cut to dimensions of 30 × 20 × 5 mm³ and polished using 1000-grit sandpaper. After the mechanical polishing, the samples underwent ultrasonic cleaning with acetone and alcohol to remove surface contaminants, followed by air drying at room temperature. The pretreated zinc blocks were heated in an alumina crucible inside a high-temperature furnace until fully melted. TiB₂-coated graphite samples were initially held above the molten zinc surface for 30 s before they were gradually immersed to mitigate the risk of coating damage due to thermal shock. Static corrosion tests were performed for the TiB₂-coated samples at a temperature of 823 K through continuous immersion for 12, 24, 72, 96, and 120 h, respectively. After the corrosion tests, the samples were removed and cooled to room temperature, and the adhering solidified zinc was preserved for further observation and analysis.

4. Characterization of nano-TiB₂ and TiB₂ coatings

The synthesized TiB₂ NPs and the cross-sectional morphologies of the TiB₂ coatings were examined using a scanning electron microscope (SEM, model: Tescan Mira3, Brno, Czech Republic) coupled with an energy dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments, Oxford, UK). Additionally, X-ray diffraction (XRD) (Rigaku Ultima IV, Tokyo, Japan, operating at 40 kV and 40 mA, with a scanning speed of 10°/min) analysis was conducted to determine the crystallographic phase composition of both the TiB₂ NPs and TiB₂ coatings. The adhesion strength of the coatings to the substrate was assessed using a Revetest Scratch Tester, an automated device for evaluating thin film adhesion, manufactured by CSM Instruments in Peseux, Switzerland. This apparatus can apply a linear load up to 100 N at a loading rate of 19.8 N/min and a scratch speed of 1 mm/min, with a fixed scratch length of 5 mm. Samples that underwent corrosion testing in molten zinc were further analyzed using SEM with an EDS detector to evaluate their surface morphology and elemental composition.

3. Results and Discussion

3.1. Test Analysis of Synthesized Nanoscale TiB₂

To explore the feasibility of generating nanoscale TiB₂ particles through the borothermal reduction of titanium dioxide in NaF-AlF₃ molten salts and to lay the groundwork for the preparation of TiB₂ coatings by electrophoretic deposition, the initial experiments focused on the borothermal reduction of nano-TiB₂ in NaF-AlF₃ molten salts. The process flowchart is illustrated in Figure 1. Following the completion of the experiment, the NaF-AlF₃ molten salt, cooled to room temperature, yielded solid salts. Subsequently, a portion of the solid salt was extracted for a comprehensive analysis using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS). The results of the tests are displayed in Figure 1b–j.

To comprehensively analyze the phase composition of the solidified salts, this study employed an XRD test, and the result is shown in Figure 1b. It is indicated that the salt was primarily composed of three substances: TiB₂, Na₃AlF₆, and Na₅Al₃F₁₄. Furthermore, the micromorphology of the solid salts was examined using SEM, as depicted in Figure 1c, showing predominantly particulate and blocky forms. Notably, a comparative elemental EDS-mapping analysis between Figure 1g,i revealed an important phenomenon: in titanium-rich areas, the oxygen content is typically lower, and these areas exhibit particulate characteristics. In conjunction with the XRD analysis, these particulate materials were identified as TiB₂. To further investigate the microstructure of the TiB₂ particles, an observation at higher magnification using SEM was conducted on the particulate materials in the rectangular area of Figure 1c, as shown in Figure 1d. By continuing to enlarge the rectangular area in Figure 1d, as shown in Figure 1e, it is evident that the size of synthesized TiB₂ particles ranges from 50 to 100 nm. It can be concluded that the borothermal reduction of titanium dioxide in NaF-AlF₃ molten salts at 1238 K successfully prepared nanoscale TiB₂ particles.

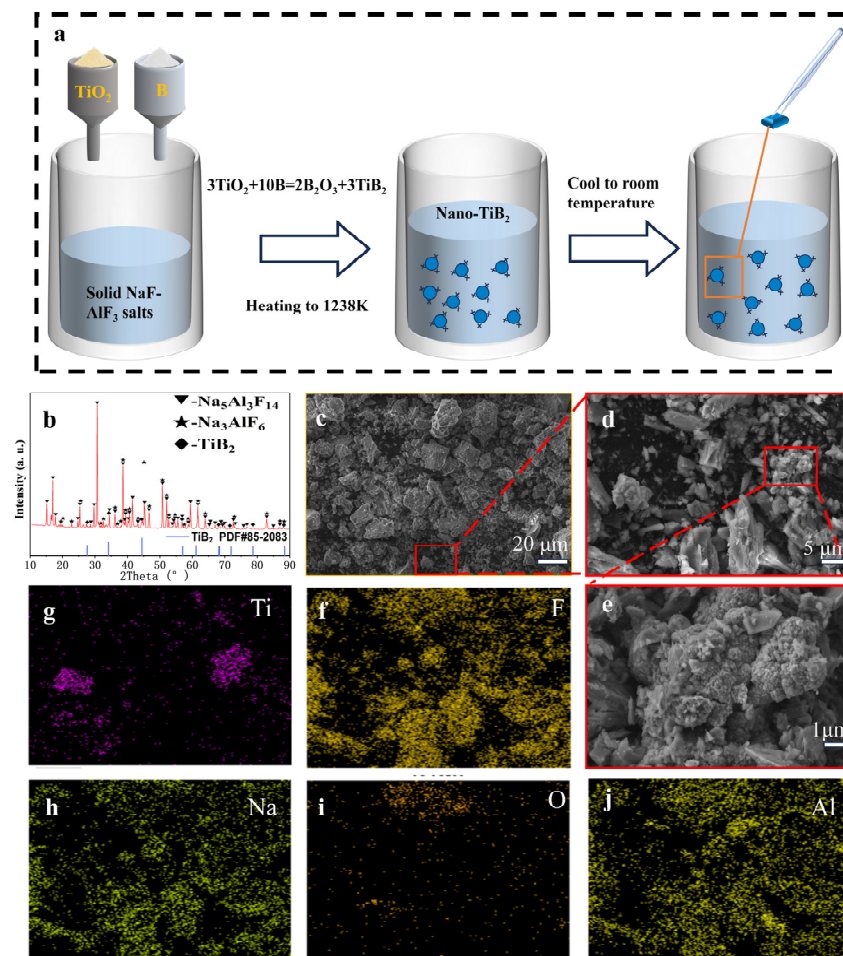


Figure 1. A schematic diagram for the preparation of nanoscale TiB_2 (a), the XRD result (b), and SEM images (c–e) of recovered TiB_2 -containing NaF-AlF_3 solid salts. Elemental EDS-mapping analysis for F, Ti, Na, O, and Al (f–j) corresponding to (c).

3.2. Test Analysis of TiB_2 Coatings on Graphite Substrates

In the prepared NaF-AlF_3 molten salts containing nanoscale TiB_2 , a constant voltage of 1.2 V was applied for 1 h to conduct the EPD experiment. The schematic diagram of the EPD process is illustrated in Figure 2a. XRD analysis confirmed that no other substances existed besides TiB_2 and C, as shown in Figure 2b. Furthermore, a detailed analysis of the cross-sectional morphology of the TiB_2 coating on the graphite substrate was conducted using SEM, with the results displayed in Figure 2c. It revealed that the TiB_2 coating has a thickness of approximately 43 μm . High-magnification SEM observations (Figure 2d) indicated that the TiB_2 coating, prepared via the MS-EPD technique, exhibits a fully dense characteristic. These results demonstrate that MS-EPD effectively prepares TiB_2 coatings, forming uniform and dense layers on graphite substrates and laying the groundwork for subsequent liquid zinc corrosion resistance testing.

Adhesion strength is defined as the maximum load that a coating can withstand without delaminating from the substrate material, and it significantly influences the service life of the coating. As illustrated in the cross-sectional images of the TiB_2 coating in Figure 2, there is a tight bond between the TiB_2 coating and graphite substrate, primarily due to the physical adhesion resulting from van der Waals forces. To quantitatively assess the adhesion strength between the TiB_2 coating and the graphite substrate, this study utilized a scratch test. The test results, shown in Figure 3, demonstrated that the initial signs of delamination in the TiB_2 coating occurred at a load of 5.4 N. Consequently, the critical load for the TiB_2 coating has been established at 5.4 N, indicating the adhesion strength

at the onset of coating failure. This adhesion strength is considered good compared to that of TiB_2 coatings prepared on graphite substrates using suspension plasma spraying technology [25].

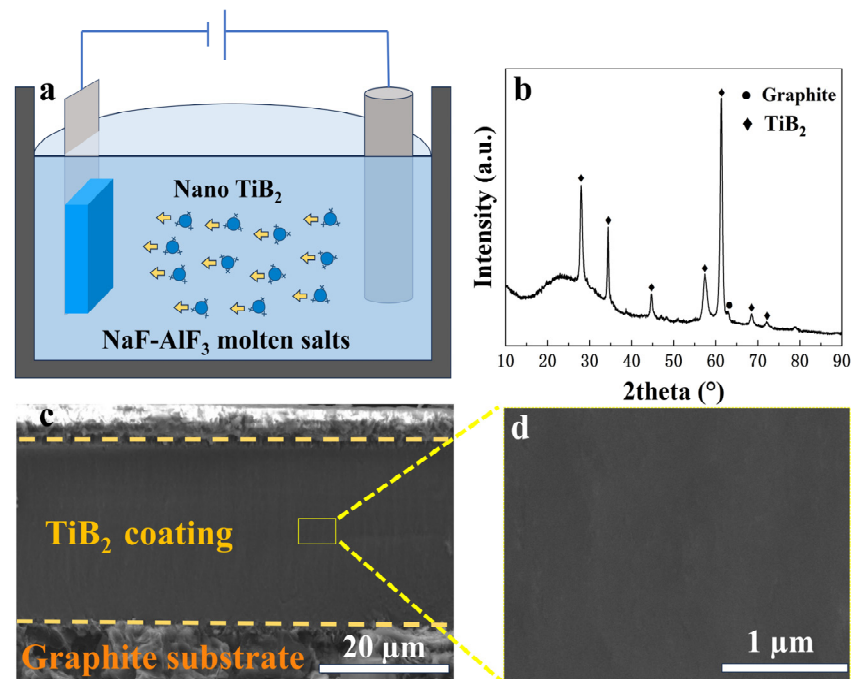


Figure 2. A schematic diagram of the MS-EPD process (a), XRD patterns obtained by EPD (b), a cross-sectional SEM image of the TiB_2 coating (c), and a high-magnification SEM image of the TiB_2 coating (d).

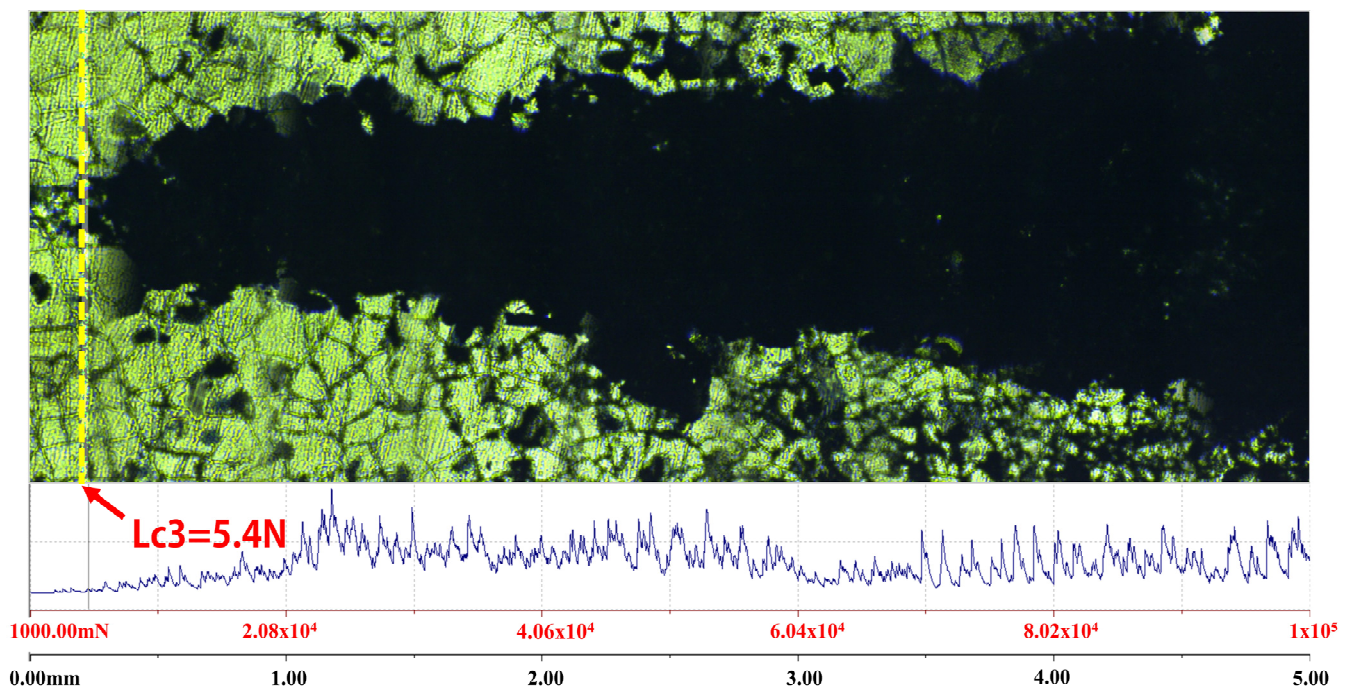


Figure 3. A scratch test for the bonding strength between the TiB_2 coating and the graphite substrate.

To investigate the interfacial characteristics between the TiB_2 coating and the graphite substrate, this study conducted linear scanning analysis and high-magnification SEM observations of the interface. The results are displayed in Figure 4. The cross-sectional

SEM images of the TiB_2 coating and the corresponding linear scanning analysis are shown in Figures 4a and 4b, respectively. These results show that there were no voids between the TiB_2 coating and the graphite substrate, indicating a good interfacial bonding intensity. Furthermore, to closely examine the interfacial bonding morphology between the TiB_2 coating and the graphite substrate, observations at higher magnification using SEM and elemental EDS-mapping tests were performed on the interface. The corresponding results are displayed in Figure 4c,d. The mapping test results demonstrate that the TiB_2 coating exhibited “rooting” growth within the pores on the surface of the graphite substrate. This growth pattern, known as “pinning growth” [26,27], enhances mechanical interlocking between the coating and substrate, thereby improving adhesion strength.

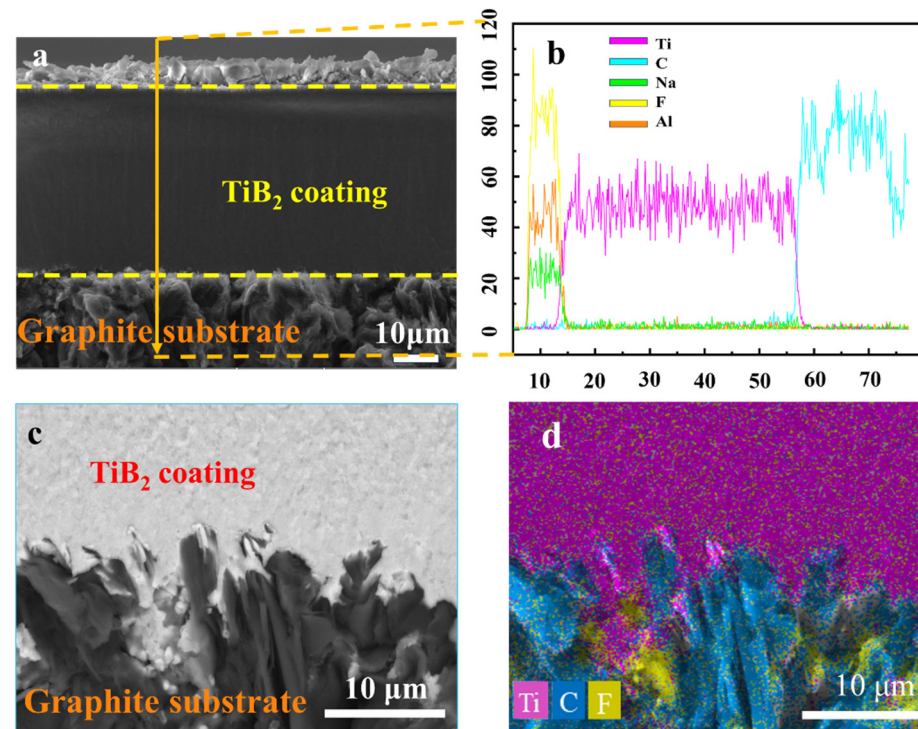


Figure 4. (a,b) Cross-sectional, low-magnification SEM image with line scan analysis. (c,d) Cross-sectional, high-magnification SEM image with corresponding elemental EDS mapping for Ti, C, and F.

3.3. Corrosion Behavior of the TiB_2 Coating in Molten Zinc

The MS-EPD technique has successfully demonstrated the fabrication of dense TiB_2 coatings on graphite substrates with excellent adhesion. To comprehensively evaluate the corrosion resistance of these TiB_2 coatings in molten zinc, a series of high-temperature immersion tests were conducted. Specifically, TiB_2 -coated samples were immersed in molten zinc at 823 K for durations of 12, 24, 72, 96, and 120 h to simulate corrosive environments over varying periods. Following the immersion tests, the TiB_2 coatings were examined with SEM and EDS to assess the corrosion conditions of their surfaces and interfaces. Figure 5 presents the corrosion test results for TiB_2 -coated samples immersed for 12, 24, and 72 h. These results are significantly important for understanding the coatings' durability in molten zinc.

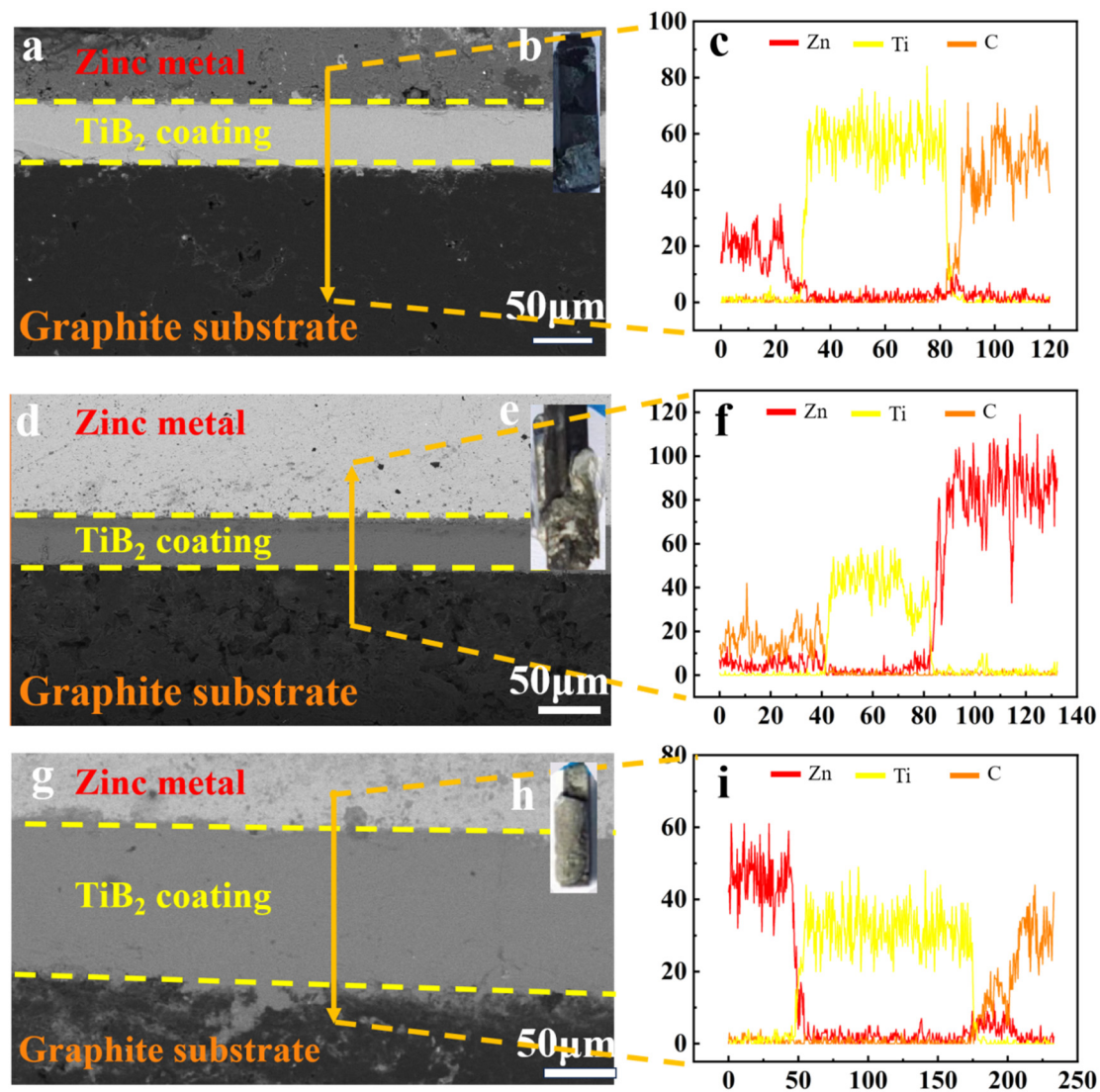


Figure 5. Cross-sectional morphology and EDS linear scan analysis results of graphite with TiB₂ coating after immersion in molten zinc for various durations: 12 h (a–c); 24 h (d–f); 72 h (g–i).

The appearance images of the TiB₂ coating after immersion in molten zinc for 12, 24, and 72 h (Figure 5b,e,h) demonstrated that the surface was uniformly encapsulated by solid zinc, suggesting good wettability between the TiB₂ coatings and molten zinc. Cross-sectional SEM images (Figure 5a,d,g) and corresponding line scan analyses (Figure 5c,f,i) revealed that the TiB₂ coatings remained intact with no corrosion damage or cracks and maintained strong adhesion to the graphite substrates after immersion for 12, 24, and 72 h in molten zinc. No new substances were detected at the interface between zinc and the TiB₂ coating. Physical adhesion was the only phenomenon observed. This indicated that no chemical reaction occurred between the TiB₂ coating and molten zinc within 72 h.

In this study, the TiB₂ coating underwent immersion in molten zinc for a prolonged period of 96 h to evaluate its long-term corrosion resistance. Figure 6a shows the cross-sectional morphology of the TiB₂ coating post-immersion, revealing an intact, dense, and continuous structure that indicates superior corrosion resistance. A magnified view of the coating's corner area (Figure 6b) further demonstrated that the TiB₂ coating effectively resists corrosion from liquid zinc. A linear scan analysis of the coating's cross-section, shown in Figure 6c, yielded results depicted in Figure 6d. The research findings show a significant reduction in zinc content near the interface between the TiB₂ coating and solid

zinc, suggesting that zinc did not significantly penetrate the TiB_2 coating through chemical reactions or diffusion over the 96 h immersion period.

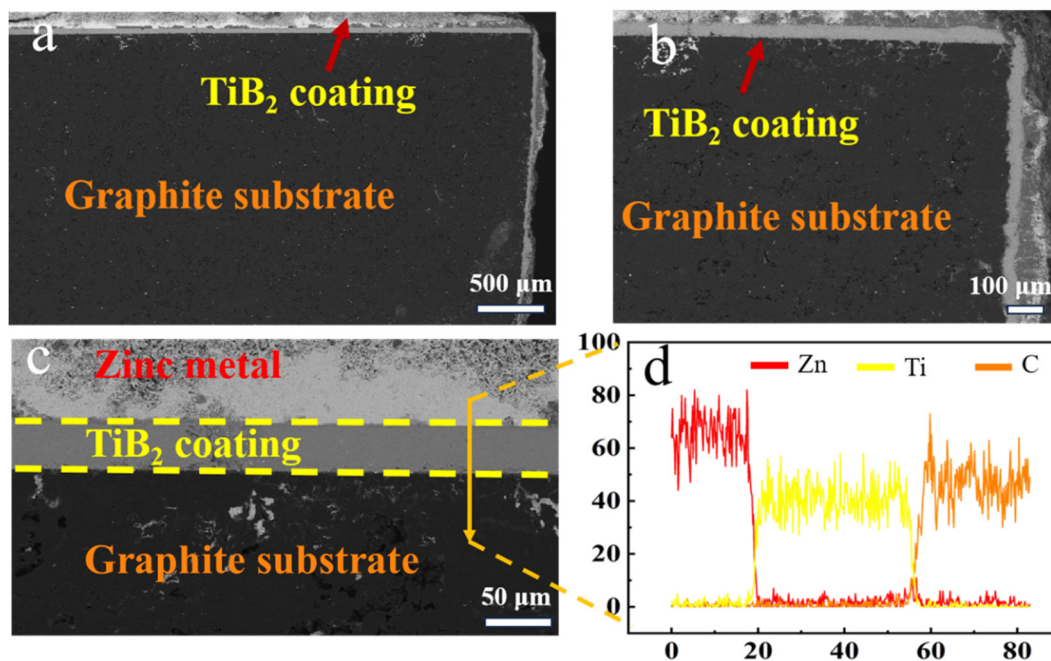


Figure 6. The corrosion resistance results of the TiB_2 coating in molten zinc (96 h). (a) A low-magnification, cross-sectional SEM image; (b) a high-magnification SEM image at the corner; (c) a high-magnification SEM image on the flat surface; (d) a line scan analysis figure.

This study extended the immersion time of the TiB_2 coating in molten zinc to 120 h to further assess its corrosion resistance. Figure 7a–c show the SEM morphologies of the TiB_2 coating cross-section after 120 h of exposure to molten zinc. The results indicate that, despite prolonged exposure to a corrosive environment, the TiB_2 coating remained crack-free and fully dense. Longitudinal linear scan results (Figure 7d) reveal that the zinc concentration at the interface between the TiB_2 coating and solid zinc sharply decreases to zero, with no overlapping distribution of titanium elements. This finding confirms the absence of significant chemical reactions or elemental diffusion between the TiB_2 coating and molten zinc. The elemental EDS-mapping analysis of the TiB_2 coating cross-section, as depicted in Figure 7c, shows no apparent mixing of titanium (Ti) and zinc (Zn) at the interface. In summary, after 120 h of immersion in molten zinc, the zinc elements did not penetrate the interior of the TiB_2 coating through chemical reactions or diffusion.

The findings of this study showed that TiB_2 coatings fabricated on graphite substrates using the MS-EPD technique exhibited exceptional corrosion resistance to liquid zinc. This superior performance is primarily attributed to two key factors. First, experimental results indicate that, at 823 K, no chemical reaction occurred between the liquid zinc and TiB_2 coating, and no new substances were detected. This confirms that the TiB_2 coating has an extremely high level of chemical stability in liquid zinc, making it capable of resisting chemical corrosion. Second, the NaF- AlF_3 molten salts demonstrated significant solubility for TiO_2 and B_2O_3 [28], a feature that facilitates the preparation of TiB_2 coatings with extremely low oxygen content through the MS-EPD technique. The low oxygen content of the coating significantly reduced the risk of intergranular corrosion, thereby further enhancing the corrosion resistance of the TiB_2 coating in liquid zinc. In summary, the combined effects of the chemical stability and low oxygen content of the TiB_2 coating confer outstanding corrosion resistance in the environment of liquid zinc.

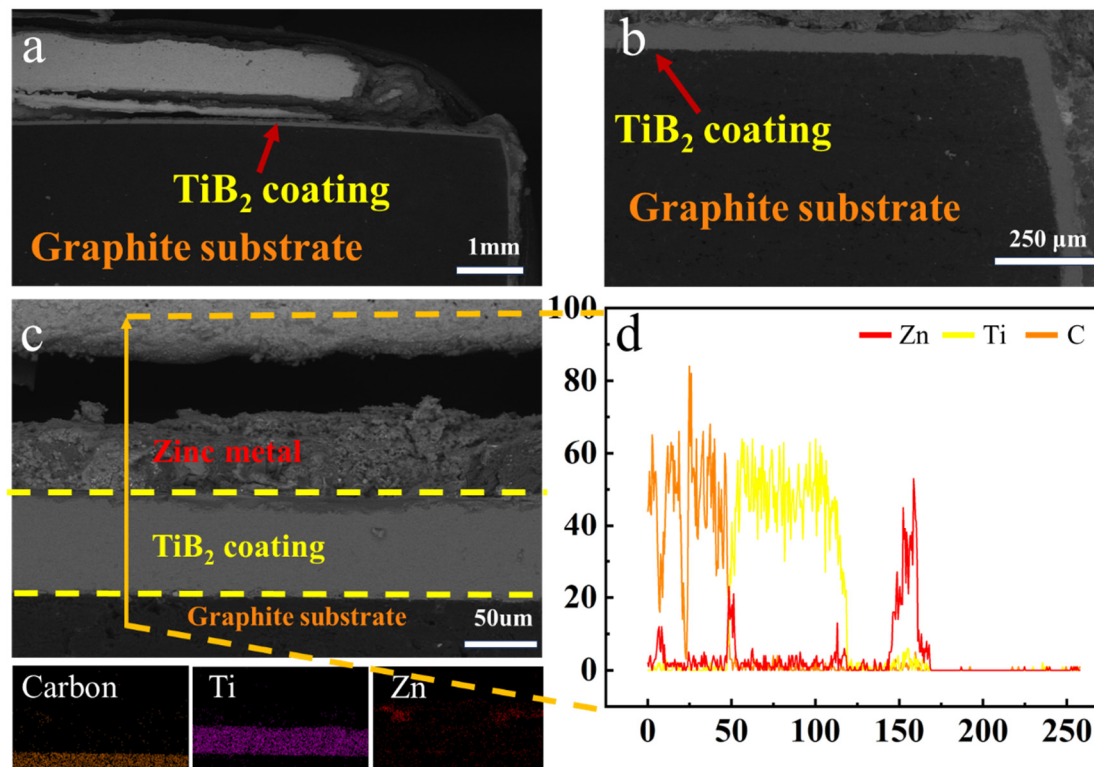


Figure 7. The corrosion resistance results of the TiB_2 coating in molten zinc (120 h). (a) A low-magnification, cross-sectional SEM image; (b) a high-magnification, cross-sectional SEM image; (c,d) cross-sectional mapping and line scan analysis images.

4. Conclusions

To broaden the potential application of TiB_2 coatings prepared by the MS-EPD technique for corrosion resistance in liquid zinc, this study not only successfully fabricated TiB_2 coatings on graphite substrates but also conducted a systematic investigation of their corrosion resistance. The main research conclusions are as follows:

1. In the NaF-AlF_3 molten salt system at 1238 K, nanoscale TiB_2 particles ranging from 50 to 100 nm were successfully synthesized via the borothermal reduction method. Applying an electrophoretic voltage of 1.2 V resulted in the deposition of these particles onto the graphite substrate, forming a TiB_2 coating with good adhesion strength (critical load $\text{Lc3} = 5.4 \text{ N}$) and a fully dense structure.
2. In the molten zinc at 823 K, no chemical reaction occurred between the TiB_2 coating and the molten zinc; the coating surface and interface remained stable. During a prolonged immersion test period of up to 120 h, excellent corrosion resistance to liquid zinc was demonstrated, which is ascribed to the corrosion-resistant TiB_2 coating, which was not only fully dense but also exhibited a low oxygen content.

Author Contributions: T.J. conducted the experiments, analyzed the data, and co-authored the manuscript. S.X. was responsible for the conception and design of the experiments, data analysis, and co-authorship of the manuscript. J.X. provided assistance in the experimental procedures related to electrophoretic deposition and in assessing the corrosion resistance of TiB_2 coatings when exposed to molten zinc. C.G. contributed to the experimental work focused on the synthesis of TiB_2 . J.P. supported the experimental efforts concerning the evaluation of the corrosion resistance of TiB_2 coatings in molten zinc. J.Z. participated in the interpretation of the results and the characterization analysis of the TiB_2 coatings. G.M.H. helped to design the experiments. All authors have read and agreed to the published version of the manuscript.

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