



Article Insight into Microstructure Evolution and Corrosion Mechanisms of K₂ZrF₆/Al₂O₃-Doped Hot-Dip Aluminum/Micro-Arc Oxidation Coatings

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Abstract: In this study, we investigated the impact of K_2ZrF_6/Al_2O_3 composite additives on the microstructure evolution and corrosion behavior of ceramic coatings formed through micro-arc oxidation (MAO) treatment on hot-dip aluminum-coated 316L stainless steel surfaces. Our findings revealed the successful preparation of micro-arc oxidation ceramic coatings, presenting a dual-layer structure consisting of a porous micro-arc oxidation ceramic outer layer and a relatively dense/thick hot-dip aluminum inner layer. The incorporation of K_2ZrF_6/Al_2O_3 composite additives induced a self-sealing effect on the ceramic coating surface. Optimal coating performance was achieved with a composite additive concentration of 7.5 g/L, resulting in remarkable improvements not only in thickness, hardness, and surface smoothness but also in corrosion resistance. This research introduces a pioneering investigation of K_2ZrF_6/Al_2O_3 composite additives in the context of micro-arc oxidation technology, offering fresh perspectives and methodologies for the development of highly corrosion-resistant materials.

Keywords: K_2ZrF_6/Al_2O_3 composite additives; micro-arc oxidation; corrosion resistance; microstructure evolution; corrosion mechanisms

1. Introduction

Solar power generation technology, being a pivotal innovation in the field of new energy generation, offers immense promise and research significance due to its attributes of high stability, operational simplicity, safety, and reliability [1-5]. Operating within the realm of solar radiation, a complex natural exposure environment, its effects extend beyond mere temperature and climate to encompass alternating cycles of dryness and humidity, as well as the pervasive presence of pollutants [6,7]. In the pursuit of a consistent electricity supply for solar power generation systems, heat storage technology plays a critical role. The choice of heat storage materials becomes not only a decision but also a determinant of their compliance with heat storage technology standards. Among the commonly utilized options are molten salts, metallic sodium, and high-temperature-resistant concrete. In addition, aluminum-based alloys offer advantages including stability, substantial heat storage capacity, and efficient thermal conductivity, making them particularly suitable for use as heat storage materials. However, elevated temperatures lead to solid-to-liquid phase transitions in these thermal storage aluminum alloys, necessitating the selection of containers characterized by commendable corrosion resistance [8,9]. Presently, container materials primarily include weathering steel and stainless steel. Nevertheless, the prolonged interaction of thermal storage aluminum alloys with containers continues to exhibit pronounced corrosive effects, posing a significant risk of safety incidents and potential disruption of



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). entire solar power generation systems if adequate measures are not taken [10–15]. Addressing this impending concern requires the prudent choice of superior container materials or the modification of container interiors to meet the practical process requirements.

In practice, addressing the challenge of severe erosion on container surfaces involves employing surface modification treatments. Among these methods, the application of hot-dip aluminum coating emerges as a robust protective measure [16,17]. The combination of thicker aluminum coatings with micro-arc oxidation (MAO) technology leads to the creation of ceramic coatings that serve as effective barriers against liquid aluminum corrosion [18–20]. However, the scope of research and application in this field remains limited, underscoring the urgent practical significance and engineering value of exploring these less-explored areas.

In the realm of MAO investigations, researchers often enhance the fundamental electrolyte by adding specific concentrations of additives to improve the characteristics of ceramic coatings. This strategic inclusion of complex oxides contributes to the formation of coatings with increased density, impressive resistance to wear and corrosion, and overall improved performance [21–24]. Among them, ZrO_2 functions as a high-temperature-resistant oxide with a high melting point, high electrical resistivity, and low thermal expansion coefficient. This makes it an ideal catalyst for enhancing high-temperature and oxidation resistance in metal devices [25–29]. Notable examples include the findings of Zhong et al. [30], which reveal the improved thermal shock resistance of MAO ceramic coatings containing zirconium dioxide, in contrast to the silica coatings formed using the solgel method. Similarly, Wang et al. [31] made significant advancements by developing MAO coatings containing ZrTiO₄ and m-ZrO₂ on the Ti6Al4V alloy, resulting in significantly enhanced oxidation resistance at elevated temperatures. The introduction of the K₂ZrF₆ compound into the basic electrolyte triggers a transformative chemical reaction within an alkaline solution, leading to the in-situ generation of ZrO₂ [32,33].

The efforts exemplified by Askarnia et al. [34] involve the application of composite coatings comprising Al_2O_3 and ZrO_2 particles onto the AZ31 magnesium alloy using MAO technology. This intervention led to a substantial reduction in surface pores, an approximately eight-fold decrease in wear rate, and a noticeable increase in coating hardness. This outcome can be attributed to the improved wettability of the coating, primarily due to Al_2O_3 . Similarly, Soliman et al. [35] conducted MAO experiments by introducing NaF and Al_2O_3 nano-additives into silicate electrolytes, resulting in a compact coating characterized by minimized roughness, primarily composed of a robust MgO phase that enhances corrosion resistance.

The above literature review suggests that introducing the K_2ZrF_6/Al_2O_3 composite additives into the basic electrolyte contributes to the presence of ZrO_2 and Al_2O_3 in the MAO coatings, thus significantly enhancing their performance [34,36,37]. However, to the best of the authors' knowledge, the impact of different concentrations of K_2ZrF_6/Al_2O_3 composite additives on ceramic coatings formed through MAO treatment of hot-dip aluminum-coated 316L stainless steel has not been investigated. Combining an outer high-performance MAO layer with the thicker aluminum layer on the 316L stainless steel has the potential to greatly improve the corrosion resistance of the developed coating system.

This innovative work was conducted using pre-prepared hot-dip aluminized stainless steel samples, optimized MAO process parameters, and a basic electrolyte. Different concentrations of composite additives, characterized by a K_2ZrF_6/Al_2O_3 composition ratio of 4/1 and designated as S0, S1, S2, S3, and S4 in ascending order, were introduced. This exploration aims to uncover the effects of varying composite additive concentrations on the characteristics of MAO ceramic coatings. The objective is to determine the optimal concentration of the composite additives that result in the highest performance of ceramic coatings.

2. Materials and Methods

2.1. Material and Coating Preparation

The 316L stainless steel material employed in this work has a dimension of 40 mm \times 13 mm \times 2 mm. This stainless steel material is produced by Shanxi Taigang Stainless Steel Co., Ltd. (Taiyuan, China). Its chemical composition (obtained through smelting analysis) is presented in Table 1.

Table 1. Main chemical composition of 316L stainless steel (in wt.%).

Element	С	Si	Mn	S	Р	Cr	Ni	Мо	Ν
Content	0.02	0.8	1.5	0.03	0.03	16.5	10.8	2.2	0.08

Pre-Treatment: The specimens were polished with sandpaper up to #1200 grit, followed by immersion in a 10 g/L NaOH solution at 80 °C for a constant 10 min. Subsequently, the surfaces were rinsed with deionized water. The specimens were then placed in a 15% HCl solution at room temperature for 5 min, followed by rinsing off the residual solution with deionized water. Next, the specimens were immersed in assist-plating agent, 5 wt.% K₂ZrF₆, at 90 °C for 15 min.

Hot-Dip Aluminum Plating: Prior to commencing the hot-dip aluminum plating experiment, standard GB 9970 aluminum granules were placed in a graphite crucible and heated in a metal melting furnace up to 1000 °C. After complete melting of the aluminum granules, the furnace temperature was lowered to 730 °C for the hot-dip aluminum plating experiment, with NaCl particles used as a covering agent. The 316L stainless steel samples were immersed in the aforementioned molten aluminum for 5 min to prepare the hot-dip aluminum layer. Subsequently, the samples were air-cooled at room temperature. The specimens were then subjected to ultrasonic cleaning for 5 min using a 5% HNO₃ + 1% HF solution, followed by ultrasonic cleaning with anhydrous ethanol for 5 min. After air-drying with cold air, the samples were stored in a drying chamber for micro-arc oxidation experiments.

Micro-Arc Oxidation Treatment: The aforementioned hot-dip plated samples underwent micro-arc oxidation treatment subsequently. A combination of silicate and phosphate electrolyte was introduced with K_2ZrF_6/Al_2O_3 composite additives at concentrations of 0 g/L (S0; 0.0 g/L $K_2ZrF_6 + 0.0$ g/L Al_2O_3), 2.5 g/L (S1; 2.0 g/L $K_2ZrF_6 + 0.5$ g/L Al_2O_3), 5.0 g/L (S2; 4.0 g/L $K_2ZrF_6 + 1.0$ g/L Al_2O_3), 7.5 g/L (S3; 6.0 g/L $K_2ZrF_6 + 1.5$ g/L Al_2O_3), and 10.0 g/L (S4; 8.0 g/L $K_2ZrF_6 + 2.0$ g/L Al_2O_3), which can be seen in Table 2. The micro-arc oxidation was performed at a frequency of 200 Hz, an oxidation time of 30 min, positive-to-negative duty ratios of 15% to 5%, and a current density of 10 A/dm².

Condition	Total Concentration (g/L)	K_2ZrF_6 (g/L)	Al_2O_3 (g/L)
S0	0.0	0.0	0.0
S1	2.5	2.0	0.5
S2	5.0	4.0	1.0
S3	7.5	6.0	1.5
S4	10.0	8.0	2.0

Table 2. The concentration of K₂ZrF₆/Al₂O₃ composite additives utilized in this work.

2.2. Characterization Methods

The micro-arc oxidation ceramic layer's surface and cross-sectional morphology were observed using a scanning electron microscope (SEM, ZEISS EVO MA15, Carl Zeiss Microscopy GmbH, Jena, Germany). Energy-dispersive X-ray spectroscopy (EDS, OXFORD 20, Carl Zeiss Microscopy GmbH, Jena, Germany) was employed to characterize the element distribution and content of the micro-arc oxidation ceramic layer on both the surface and cross-sectional surface. X-ray diffraction (XRD) analysis was carried out on a DX-2700B diffractometer (Dandong Haoyuan Instrument Co., Ltd., Dandong, China) for phase composition analysis of the micro-arc oxidation ceramic layer. Specific parameters were as follows: Cu target, K α radiation source, acceleration voltage and current set at 40 kV and 40 mA, respectively, step size of 0.0167°, dwell time of 12 s, approximately 0.1°/min.

The thickness of the aluminum coating under different plating temperatures and times, as well as the thickness of the micro-arc oxidation ceramic layer with varying concentrations of composite additives, was measured using the TT-230 eddy current thickness gauge, with an accuracy of 1 μ m. For each test, five random positions on the aluminum-coated surface were selected, and the average of the measurements was taken as the final thickness value. The surface hardness of the micro-arc oxidation ceramic layer doped with different concentrations of composite additives was measured using a digital micro-hardness tester (HXD-1000TMB, Shanghai Taiming Optical Instrument Co., Ltd., Shanghai, China), with a loading force of 100 gf, a holding time of 15 s, and a diamond indenter. Similarly, five random positions on the ceramic layer surface were chosen for each test, and the average of the measurements value.

The corrosion resistance of the micro-arc oxidation ceramic layer was analyzed using an electrochemical workstation (Reference 3000, Gamry, Philadelphia, PA, USA). Employing the classical three-electrode system, the specimen served as the working electrode, a platinum electrode as the auxiliary electrode, and a saturated calomel electrode as the reference electrode. For electrochemical impedance spectroscopy, the specific technical parameters were as follows: test area of 1 cm², frequency range from 100 kHz to 0.01 Hz, and amplitude set at \pm 10 mV. All electrochemical tests were conducted in a 5% NaCl solution at room temperature of 25 °C.

3. Results and Discussion

3.1. Analysis of Oxidation Voltage in Micro-Arc Oxidation Process

Figure 1 demonstrates that the relationship between oxidation voltage and time during the micro-arc oxidation (MAO) experiment exhibits a consistent pattern across various additive concentrations. In the early stage of the MAO process (i.e., 0–3 min), the oxidation voltage rises linearly and rapidly with time, with nearly identical growth rates among different composite additive concentrations. At this phase, the oxidation voltage has not yet reached the critical breakdown voltage, as shown in the image. It is found that gas bubbles begin to emerge around the anode sample, and the temperature gradually ascends. As time elapses (i.e., 3–5 min), the growth rate of the oxidation voltage decelerates. Concurrently, a handful of sparks appear on the sample's surface, accompanied by an escalation in temperature. Subsequently (i.e., 5–20 min), the oxidation voltage stabilizes at a specific value. This signifies the appearance of numerous volcano-like micropores on the sample's surface, penetrated by the oxidation voltage, leading to an intensification and brightening of the sparks [38,39].

Moreover, during the MAO process, as the concentration of composite additives increases, the oxidation voltage follows a pattern of initial increase and subsequent decrease. Remarkably, at a concentration of 7.5 g/L, the oxidation voltage reaches its peak at 530 V. This behavior is primarily due to lower additive concentrations at which K_2ZrF_6 and Al_2O_3 disperse in the electrolyte. Hydrolysis could lead to the formation of Al(OH)₃ and Zr(OH)₄ precipitates, which further hinder the movement of charged particles in the electrolyte. This elevation in electrolyte resistance necessitates a higher oxidation voltage to induce surface breakdown [40]. Consequently, within the additive concentration. However, with a further increase in additive concentration, agglomeration occurs during the formation of the ceramic layer. This obstructs the progression of the MAO process, leading to a slowdown in coating deposition rates and, consequently, a reduction in surface resistance. As a result, when the additive concentration reaches 10 g/L, the oxidation voltage displays a declining trend.



Figure 1. U-T (oxidation voltage–time) variation curve of hot-dip aluminum plated samples with composite additives at different concentrations during the micro-arc oxidation treatment.

3.2. Microstructure and Elemental Analysis of Micro-Arc Oxidation Ceramic Coatings

Figure 2 presents the surface morphology and elemental distribution of ceramic coatings formed through micro-arc oxidation treatment on hot-dip aluminum-coated 316L stainless steel surfaces, with varying concentrations of K_2ZrF_6/Al_2O_3 composite additives introduced into an optimized silicate-phosphate-based electrolyte. As seen in the figures, a layer of micro-arc oxidation ceramic coating was successfully prepared on the surface of the 316L hot-dip aluminum-coated samples, characterized by numerous discharge micropores and a typical volcanic morphology. EDS mapping reveals a relatively uniform distribution of O, Al, and Zr elements in the ceramic coatings, indicating the successful involvement of Zr elements in the formation of the micro-arc oxidation coating. During the micro-arc oxidation process, Zr mainly exists in the form of ZrO₂, which has been reported to significantly enhance heat shock resistance and oxidation resistance of micro-arc oxidation coatings [41]. In this work, the addition of K_2ZrF_6 may induce the generation of ZrO₂, possibly following the following mechanism [41]:

$$K_2 ZrF_6 \rightarrow 2K^+ + ZrF_6^{2-} \tag{1}$$

$$\operatorname{ZrF_6}^{2-} + 4\operatorname{OH}^- \to \operatorname{Zr}(\operatorname{OH})_4 + 6\operatorname{F}^-$$
 (2)

$$Zr(OH)_4 \to ZrO_2 + 2H_2O \tag{3}$$

$$\operatorname{ZrF_6}^{2-} + 4\operatorname{OH}^- \to \operatorname{ZrO_2} + 6\operatorname{F}^- + 2\operatorname{H_2O}$$
 (4)

From Figure 2a, it is evident that at a composite additive concentration of 2.5 g/L, there are larger and numerous discharge micropores on the ceramic coating surface. This is primarily due to the fusion of adjacent micropores during the micro-arc oxidation process, resulting from the abundance of micropores. As the composite additive concentration increases to 5 g/L (Figure 2b), the Al_2O_3 and K_2ZrF_6 powders partially fill the micropores, reducing their quantity. This enhances the coating's surface density and smoothness while generating a small amount of white fusion material. Based on EDS mapping results

and previous studies, this white fusion material is mostly composed of silicon–oxygen compounds. Excessive silicon–oxygen compounds can affect the smoothness of the ceramic coating surface. At a composite additive concentration of 7.5 g/L (Figure 2c), the ceramic coating surface becomes smoother, with fewer white fusion materials, and many micropores are covered by fine particles. However, when the composite additive concentration reaches 10 g/L (Figure 2d), more white fusion materials are generated on the ceramic coating surface, and there are more micro-convex regions. This suggests that an excessively high composite additive concentration can reduce the surface smoothness of the ceramic coating and affect the coating's performance.



Figure 2. Surface micromorphology and element distribution of ceramic coating on hot-dip aluminized samples after micro-arc oxidation treatment under different composite additive concentrations: (**a1**) 2.5 g/L; (**b1**) 5.0 g/L; (**c1**) 7.5 g/L; (**d1**) 10 g/L; (**a2–d2**) is the enlarged image of the corresponding area).

According to Table 3, the ceramic coating contains a series of elements including O, Al, P, Zr, and Si. With the increase in composite additive concentration, the Zr content also increases, indicating the increasing involvement of Zr elements in the film-forming process. This confirms the presence of ZrO_2 on the coating surface. Additionally, the Si content exhibits a trend of initially decreasing and then increasing. When the composite additive concentration is 7.5 g/L, the Si content is the lowest, at only 0.8 wt.%, consistent with the SEM results mentioned above. This indicates that at this concentration, there are fewer white fusion materials, and the ceramic coating's surface smoothness and density are optimal.

Table 3. EDS element content on the surface of hot-dip aluminized samples after micro-arc oxidation treatment under different composite additive concentrations.

Composite Additive Concentration (g/L)	O (wt.%)	Al (wt.%)	P (wt.%)	Si (wt.%)	Zr (wt.%)
2.5	35.165	61.538	0.200	1.399	1.698
5.0	31.900	64.900	0.300	1.100	1.800
7.5	30.400	66.300	0.300	0.800	2.200
10.0	30.800	65.500	0.300	1.100	2.300

Figure 3 illustrates the cross-sectional morphology and elemental linear distribution of hot-dip aluminum-coated samples after micro-arc oxidation treatment at different composite additive concentrations. As shown, the coating structure is dense, without distinct porous layers. According to the linear element scanning results, in the vicinity of the outer surface (0–10 μ m), the content of Al, Zr, and O is higher. However, beyond this depth, the Al content is high, while the Zr and O contents are lower. This indicates a layered structure of the coating, with the outer layer being rich in Al, Zr, and O, mainly constituting an Al₂O₃-ZrO₂ micro-arc oxidation layer. The inner layer is rich in Al, mainly derived from the hot-dip plating process. Furthermore, Si elements tend to randomly aggregate throughout the entire coating thickness.



Figure 3. Cross-sectional morphology and element distribution of hot-dip aluminized samples after micro-arc oxidation treatment under different composite additive concentrations: (**a**) 2.5 g/L; (**b**) 5.0 g/L; (**c**) 7.5 g/L; (**d**) 10 g/L.

3.3. Phase Analysis of Micro-Arc Oxidation Ceramic Coatings

Figure 4 shows the XRD spectra of samples after micro-arc oxidation treatment of hot-dip aluminum-coated 316L stainless steel surfaces with varying concentrations of composite additives. From the graph, it can be observed that the diffraction peaks are mainly attributed to Al and Al₂O₃ phases. The presence of characteristic peaks of Al indicates that the micro-arc oxidation ceramic coating is relatively thin, allowing X-rays to easily penetrate the ceramic coating during testing and detect the aluminum plating layer on the stainless steel substrate. Additionally, the intensity of the Al characteristic peak is highest in sample S1, indicating a thinner micro-arc oxidation coating and easier detection of the aluminum plating layer by X-rays. As the composite additive concentration increases, the intensity of the Al characteristic peak decreases, suggesting that higher concentrations of composite additives can effectively increase the thickness of the ceramic coating. The Al_2O_3 phase in the XRD spectra exhibits a single characteristic peak, and the intensity of this peak remains relatively consistent across different additive concentrations. This indicates that its origin is primarily the oxidation of aluminum atoms in the aluminum plating layer during the micro-arc oxidation process, although Al₂O₃ powder in the additives could also contribute to its presence. Furthermore, no ZrO_2 was detected, suggesting that the content of ZrO_2 is relatively low and exists only near the surface of the coating, as confirmed by SEM and EDS results. It should be noted that the diffraction peak of Al deviates from the standard position of the Al peak and shifts slightly to the right [37,42,43]. The occurrence of this peak shift phenomenon indicates a distortion in the lattice constant of the Al crystal during the processes of hot-dip coating and micro-arc oxidation [44–46]. This phenomenon may be related to the presence of residual stresses, or compounds such as Al₂O₃, ZrO₂, or SiO₂. However, the specific reasons for this need further in-depth research.



Figure 4. XRD patterns of hot-dip aluminized samples after micro-arc oxidation treatment under different composite additive concentrations.

3.4. Analysis of Thickness and Hardness of Micro-Arc Oxidation Ceramic Coatings

In general, there are two main factors influencing the corrosion resistance of ceramic coatings during the micro-arc oxidation process. Firstly, the microstructure of the ceramic

coating's surface plays a significant role. Variations in the number and non-uniformity of unique volcano-like micropores on the surface of micro-arc oxidation ceramic coatings lead to different probabilities of corrosion ions diffusing through these micropores and reaching the interface of the intermediate layer or substrate. A higher number and larger size of micropores facilitate the diffusion of corrosive ions to the substrate interface, resulting in poorer corrosion resistance [47–53]. Secondly, the thickness and hardness of the ceramic coating are also important factors affecting the corrosion resistance of composite coatings. Thicker ceramic coatings provide a greater barrier against corrosive ions for the intermediate layer or substrate interface [54]. The hardness of micro-arc oxidation coatings directly impacts their corrosion resistance [55]. A higher coating hardness usually indicates better resistance against scratching, wear, and deformation, thereby reducing the susceptibility of the coating to external erosive forces.

According to Figure 5a, it can be observed that with an increase in the concentration of composite additives, the thickness of the ceramic coating initially increases and then decreases, reaching its maximum value at 7.5 g/L. This indicates that incorporating K_2ZrF_6/Al_2O_3 composite additives into the base electrolyte within the range of 0 to 7.5 g/L promotes an increase in the thickness of the ceramic coating. The primary reason for this is that the addition of K_2ZrF_6/Al_2O_3 composite additives alters the oxidation voltage during the micro-arc oxidation process, which is directly related to the deposition rate of the coating. Higher oxidation voltage leads to a faster deposition rate and, consequently, a thicker coating, aligning with the conclusions drawn from Figure 1. However, when the concentration of composite additives reaches 10 g/L, the reduction in the thickness of the ceramic coating can be attributed to the uneven diffusion of excessive additives within the electrolyte. This can lead to aggregation and adhesion on the surface of the hot-dip aluminum-coated samples, making it more difficult to breach the aluminum plating layer and impeding the arc discharge during the micro-arc oxidation process, thereby affecting the coating's deposition rate.



Figure 5. Thickness value (**a**) and hardness value (**b**) of ceramic coating on hot-dip aluminum-coated samples after micro-arc oxidation treatment under different composite additive concentrations.

From Figure 5b, it can be seen that the trend in hardness variation of the ceramic coating corresponds closely with the thickness variation trend. This implies that the microarc oxidation ceramic layer significantly contributes to the hardness value. When 7.5 g/L of K_2ZrF_6/Al_2O_3 composite additives are added, the hardness value of the sample increases from 406HV to 482HV compared to the sample without K_2ZrF_6/Al_2O_3 additives. The increase in coating hardness can be attributed to the addition of 7.5 g/L K_2ZrF_6/Al_2O_3 , which significantly enhances the oxidation voltage during the micro-arc oxidation process as evidenced by Figure 1. This, in turn, provides more oxidation energy, leading to the formation of more hard phases such as Al_2O_3 and ZrO_2 . The presence of these hard phases contributes to the improved surface hardness of the coating.

3.5. Electrochemical Response and Corrosion Mechanism Analysis

Electrochemical methods play a crucial role in evaluating the corrosion performance of micro-arc oxidation coatings. These methods simulate the electrochemical processes in real corrosion environments, providing comprehensive and quantitative information about coating corrosion performance [45,52,56,57]. Among these methods, electrochemical impedance spectroscopy (EIS) plays a pivotal role in analyzing the corrosion performance of micro-arc oxidation coatings. EIS data present the electrochemical impedance spectrum of the coating, encompassing various aspects such as charge transfer processes, interfacial reactions, and the formation of corrosion products. These data not only aid in a deeper understanding of corrosion types and degrees but also predict the durability and lifespan of coatings in practical use.

As shown in Figure 6a, Nyquist plots and low-frequency area magnifications of microarc oxidized coatings on hot-dip aluminum-coated samples under different composite additive concentrations exhibit similar electrochemical behavior. Generally, the relationship between resistance and capacitance in charge transfer processes can be reflected by the impedance arc in Nyquist plots. The size of the impedance arc's radius is directly proportional to the corrosion resistance of the sample; a larger radius indicates better corrosion resistance [45,57–59]. From the magnified low-frequency area, it can be observed that the impedance arc radius of ceramic coatings on hot-dip aluminum-coated samples increases initially and then decreases with the rise in composite additive concentration. The S3 sample has the largest impedance arc radius, indicating the best corrosion resistance. The corrosion resistance order can be listed as follows: S3 > S4 > S2 > S1 > S0. The poorest corrosion resistance is observed in S0 samples, confirming that the K₂ZrF₆/Al₂O₃ composite additives used in this study effectively enhance the corrosion resistance of micro-arc oxidation ceramic coatings.

Figure 6b presents Bode plots of micro-arc oxidized coatings on hot-dip aluminumcoated samples after treatment under different composite additive concentrations. The corrosion resistance of samples can also be evaluated by the magnitude of |Z| at low frequency; larger |Z| values indicate better corrosion resistance. It can be confirmed that the S3 sample exhibits the best corrosion resistance. Additionally, the phase angle and impedance values of all samples change in a similar trend as frequency varies, suggesting that K₂ZrF₆/Al₂O₃ composite additives only influence the corrosion resistance of the microarc oxidation ceramic coating and do not alter the structural characteristics of the ceramic layer itself [60]. Furthermore, the Bode plots reveal at least two time constant features, corresponding to the ceramic outer layer of the coating and the hot-dip aluminum inner layer, aligning with the cross-sectional analysis results.

Figure 7 illustrates the equivalent circuit diagram of EIS for micro-arc oxidized coatings on hot-dip aluminum-coated samples after treatment under different composite additive concentrations. In the diagram, R_s represents the electrolyte resistance, R_{P1} and C_{P1} represent the equivalent resistance and capacitance of the outer layer of the coating, while R_{P2} and C_{P2} represent the equivalent resistance and capacitance of the inner layer of the coating. The ZSimpWin impedance spectroscopy fitting software was employed to fit EIS data, and the fitted parameters are presented in Table 4. It can be observed that the fitted resistance $R_{P2} > R_{P1}$. This is due to the thicker hot-dip aluminum inner layer, which better resists the corrosion of external corrosive ions, resulting in higher impedance values. Conversely, the micro-arc oxidation outer layer of the coating is thinner and contains certain voids, facilitating the passage of corrosive ions and thus leading to relatively lower impedance values. Nevertheless, research indicates that porous ceramic coatings can exhibit a self-sealing effect during the corrosion process, effectively preventing further corrosion. The self-sealing effect of micro-arc oxidation coatings refers to the ability of small pores on the coating surface to close, enhancing the coating's sealability and corrosion resistance. Methods for achieving self-sealing pores in micro-arc oxidation coatings generally involve optimizing process parameters, increasing oxide film thickness, implementing secondary treatments, adding pore-sealing agents, utilizing surface treatments, etc. These methods aim

to reduce pore formation and promote the self-filling and sealing of internal coating pores, thereby enhancing the sealability and corrosion resistance of the coating. Additionally, the appearance of an additional time constant in the high-frequency position of the Bode plots might be attributed to further self-sealing effects of the coating. Similar reports are found in the literature [61].



Figure 6. EIS spectra of micro-arc oxidation coatings on hot-dip aluminum-coated samples treated under different composite additive concentrations: (**a**) Nyquist plot; (**b**) Bode plot.



Figure 7. Equivalent circuit diagrams of EIS for micro-arc oxidation coatings on hot-dip aluminumcoated samples treated under varying composite additive concentrations.

Table 4. Fitting results of EIS for micro-arc oxidation coatings on hot-dip aluminum-coated samples treated under different composite additive concentrations.

Sample	R_s ($\Omega \cdot cm^2$)	C_{p1} (F·cm ⁻²)	R_{p1} ($\Omega \cdot cm^2$)	$C_{p2} (F \cdot cm^{-2})$	R_{p2} ($\Omega \cdot cm^2$)
S0	20.37	$9.707 imes 10^{-5}$	545.3	$3.856 imes 10^{-3}$	1134
S1	14.56	$1.746 imes10^{-4}$	580.0	2.871×10^{-3}	1353
S2	52.13	$2.242 imes 10^{-5}$	1473.0	$1.430 imes 10^{-3}$	2779
S3	52.70	$1.263 imes10^{-5}$	3240.0	$6.439 imes10^{-4}$	7488
S4	18.26	$7.745 imes 10^{-7}$	2571.0	$3.112 imes 10^{-5}$	3207

With an increase in the concentration of K_2ZrF_6/Al_2O_3 composite additives, both R_{P1} and R_{P2} show an initial increase followed by a subsequent decrease. The combined value of R_{P1} and R_{P2} determines the level of the coating's resistance to external corrosion. Consequently, the corrosion resistance of the film layer demonstrates an initial improvement, followed by a reduction. The S3 sample exhibits the highest R values, reaching 3240 $\Omega \cdot cm^2$ and 7488 $\Omega \cdot cm^2$ respectively, indicating the best corrosion resistance among the samples. This suggests that an appropriate amount of K_2ZrF_6/Al_2O_3 powder adequately fills the volcano-like micropores on the micro-arc oxidation ceramic coating, reducing the number and size of these pores [56,61,62]. Moreover, the formed phases such as Al_2O_3 and ZrO_2 can obstruct the erosion of corrosive ions, enhancing the corrosion resistance of the ceramic coating [63,64].

In summary, K_2ZrF_6/Al_2O_3 composite additives were introduced into the micro-arc oxidation technology field in this investigation, revealing their impact on ceramic coating performance and corrosion resistance. This research not only advances the forefront of micro-arc oxidation technology but also provides new perspectives and methodologies for exploring the realm of material corrosion and protection.

4. Conclusions

This study investigated the influence of introducing different concentrations of K_2ZrF_6/Al_2O_3 composite additives into an optimized silicate–phosphate-based electrolyte on the microstructure evolution and corrosion mechanism of ceramic coatings formed on the surface of 316L stainless steel through hot-dip aluminum coating and subsequent micro-arc oxidation (MAO) treatment. The specific conclusions are as follows:

(1) The analysis of oxidation voltage in the micro-arc oxidation process revealed consistent patterns across various additive concentrations of $K_2 ZrF_6/Al_2O_3$. However, increasing additive concentrations led to an initial rise and subsequent decline in the stabilized oxidation voltage, with the maximum value found at a concentration of 7.5 g/L.

(2) Micro-arc oxidation ceramic coatings were successfully prepared on the surface of 316L stainless steel hot-dip aluminum-coated samples, forming a dual-layer structure

of hot-dip aluminum/micro-arc oxidation ceramic coating. The micro-arc oxidation ceramic coating primarily consisted of Al_2O_3/ZrO_2 and displayed numerous micropores. The addition of K_2ZrF_6/Al_2O_3 composite additives resulted in a self-sealing effect on the ceramic coating surface, simultaneously impacting the coating properties. With an increase in composite additive concentration, the thickness and hardness of the ceramic coating showed an initial increase followed by a decrease trend. When the composite additive concentration reached 7.5 g/L, both the thickness and hardness of the ceramic coating reached their maximum values. Additionally, the coating surface became smooth and compact, effectively retarding the penetration of corrosive media and significantly enhancing corrosion resistance.

(3) Electrochemical results supported that the coating on the sample surface exhibited a dual-layer structure, mainly composed of a porous micro-arc oxidation ceramic outer layer and a relatively thick hot-dip aluminum inner layer. When the $K_2 ZrF_6/Al_2O_3$ composite additive concentration was 7.5 g/L, the resistance values of both the inner and outer layers reached their maximum values, indicating that the hot-dip aluminum/MAO ceramic coating possessed the best corrosion resistance.

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