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Study on Growth and Corrosion Resistance of Lanthanum Salt Conversion Film on Galfan Surface by Hot Dip Plating in Power Transmission and Transformation Engineering

Guanliang LU[1], Linkun YUAN, Ruobing HE, Chunhong CHEN and Jianfang LAI
Yangjiang Power Supply Bureau of Guangdong Power Grid Co., Ltd., Yangjiang City, Guangdong Province, 529500, China.

Abstract. Hot dip plating is a widely used metal surface treatment process, which can provide protection and enhancement of metal surfaces and is suitable for electric power fields. The surface of hot-dip Galfan coatings was prepared with lanthanum salt conversion film. A comprehensive investigation was conducted using various characterization techniques, including scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). Additionally, the corrosion resistance of the film was studied through neutral salt spray tests, electrochemical polarization analysis, and electrochemical impedance spectroscopy, and the optimal film-forming time was determined. Based on the above research, it can be concluded that lanthanum salt conversion films significantly enhance the corrosion resistance of hot-dip Galfan coatings, particularly in transmission and transformation engineering. This contributes to further improving the performance and stability of the coatings.

Keywords. Power transmission and transformation engineering; hot dip Galfan; conversion film; lanthanum salt; growth mechanism; corrosion resistance

1. Introduction

Hot dip plating is a common metal surface treatment process, which is usually used to protect the metal surface from corrosion and oxidation [1-2]. With the diversification of application fields of hot dip coating products and the improvement of corrosion resistance requirements, zinc-aluminum alloy coating, as a new coating material, has great development potential and broad application prospects [3].

To enhance the corrosion resistance of coatings used in power transmission and transformation engineering, the metal surfaces are typically subjected to chromate passivation treatment[4]. However, hexavalent chromium is highly toxic and can pose serious hazards to the environment and human health, thus subject to strict restrictions. In recent years, scholars both domestically and internationally have been devoted to researching chromium-free passivation technologies. These technologies mainly include

[1] Corresponding author: 2129867268@qq.com

inorganic passivation, organic passivation, and composite passivation. Among them, rare earth passivation has attracted significant attention due to its non-toxic, non-polluting nature, and excellent corrosion resistance properties. Researchers have found that rare earth salts exhibit significant corrosion inhibition effects on zinc alloys [5-6].

Currently, there is limited research on rare earth conversion coatings on the surface of Galfan coatings both domestically and internationally. This study utilizes La(NO3)3·6H2O as the primary salt to prepare lanthanum conversion coatings on the surface of Galfan coatings. Through techniques such as SEM and XPS, the surface morphology, chemical composition, and structure of the coatings are investigated to analyze the growth process of the coatings. Additionally, neutral salt spray tests (NSS), electrochemical polarization curves, and electrochemical impedance spectroscopy (EIS) are employed to evaluate the corrosion resistance performance of the coatings.

2. Experimental method

The pretreatment conditions include: degreasing with a 15 % NaOH hot alkaline solution, followed by hot water rinsing, rust removal with a 15 % HCl acid solution, cold water rinsing, application of a plating aid, and drying. After pretreatment, the samples are placed in a graphite crucible (SG2-7.5-10) containing molten Galfan (Zn-5% Al-0.1 % RE by mass fraction) for hot-dip galvanizing. LEO1530VP scanning electron microscope (SEM) and Inca300 energy dispersive spectrometer (EDS) were used to analyze the microstructure and chemical composition of the film. Surface morphology and composition

Figure 1 illustrates the surface morphology of hot-dip Galfan samples treated with lanthanum salt conversion solution for 10 s to 60 min, as observed by SEM. As the treatment time increases, the lanthanum salt conversion film gradually accumulates and protrudes near grain boundaries and phase boundaries, eventually forming a continuous coating. However, when the treatment time reaches 60 min, the coating begins to peel off, resulting in the surface of the sample splitting into two layers, with newly formed coating observed in the peeled areas. This phenomenon suggests the dynamic evolution of the lanthanum salt conversion film with varying treatment durations.

The morphology and elemental composition differences between the lanthanum salt conversion film on Galfan surfaces prepared through hot-dip plating and untreated surfaces were compared using SEM and EDS analysis. SEM analysis revealed that, with increasing treatment time, the lanthanum salt conversion film gradually accumulates and protrudes near grain and phase boundaries, eventually forming a continuous coating. EDS results indicated that the conversion film mainly consists of Zn, Al, O, and La elements. As the treatment time increases, the content of Zn decreases, the content of Al initially increases then decreases, while the content of La increases, suggesting an increase in film thickness over time. Moreover, compared to flat areas, the accumulation areas of the film layer exhibit higher contents of La and O, but lower contents of Zn and Al, indicating uneven film formation. When the treatment time reaches 60 minutes, the coating begins to peel off, causing the surface of the sample to split into two layers, with a newly formed coating observed in the peeled areas. These observations indicate significant differences in the morphology and elemental composition of the lanthanum salt conversion film compared to untreated surfaces, and the formation and stability of the conversion film are closely related to the treatment time.

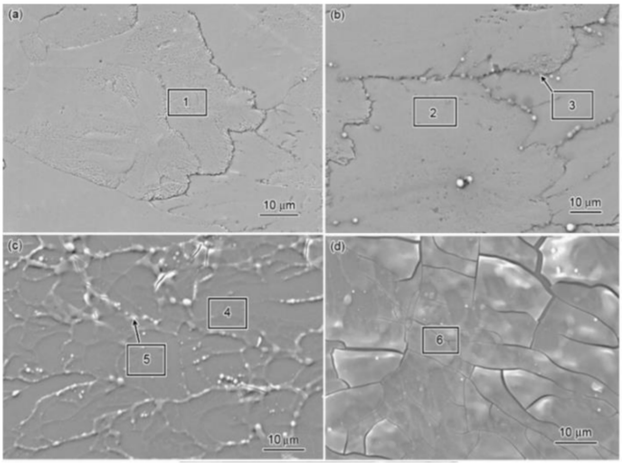

Figure 1. SEM images of lanthanum salt conversion films with different treatment time

Table 1's EDS analysis reveals that the lanthanum salt conversion film on Galfan surfaces mainly comprises Zn, Al, O, and La, with treatment time leading to a reduction in Zn, an initial increase followed by a decrease in Al, and an increase in La, suggesting the film's thickening over time. The analysis also shows uneven film formation, highlighted by higher La and O contents in accumulation areas than in flat areas, and the absence of La and Al in areas where the film has peeled off after 60 minutes of treatment.

Analytical area	Treatment time	Zn	Al	O	La
1	10 s	88.12	11.88	-	-
2	1 min	72.01	13.82	13.71	0.46
3	1 min	49.58	12.05	36.22	2.15
4	10 min	49.52	7.71	39.34	3.43
5	10 min	16.04	2.54	68.91	12.50
6	30 min	34.07	1.57	54.07	10.29
7	60 min	8.96	1.07	72.92	17.05
8	60 min	89.05	10.95	-	-

Table 1. EDS analysis results of each micro-area in the figure. 1

2.1. X-ray photoelectron spectroscopy, XPS analysis

Figure 2 illustrates the compositional analysis at various depths from the surface of the sample treated for 1 minute. As depicted in the figure, the coating's surface exhibits elevated levels of Al, La, and O elements, with the Al content initially increasing and then decreasing along the depth direction before reaching stability. In contrast, both La and O contents gradually decrease with increasing depth. Conversely, the surface Zn content is relatively low but shows a gradual increase with depth. This suggests that, under short-term treatment conditions, film formation is primarily attributed to the deposition of Al(OH)3/Al2O3 and La(OH)3/La2O3.

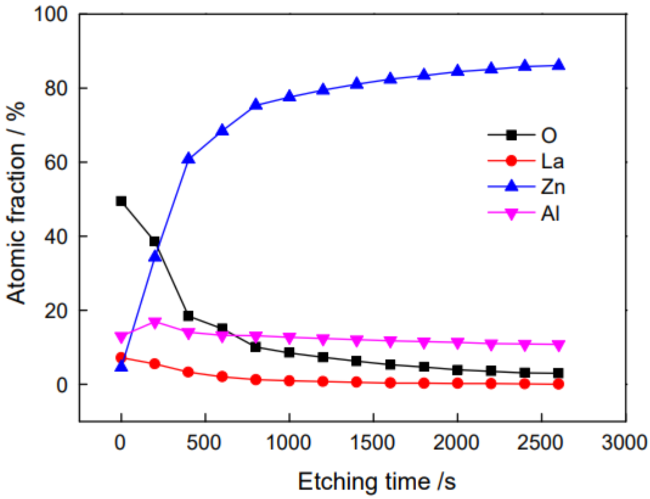

Figure 2. XPS depth analysis chart with processing time of 1 min

XPS analysis reveals that the predominant chemical states of lanthanum on the surface of the Galfan coatings, after undergoing the conversion process, are predominantly in the form of La(III) oxides/hydroxides. The La(III) species, identified through the analysis, include La2O3 and possibly La(OH)3, which are known for their protective properties and ability to form dense and stable conversion coatings on metal surfaces. These lanthanum compounds effectively act as a barrier against corrosion by providing a protective layer that reduces the direct exposure of the underlying metal to corrosive environments.

Moreover, the presence of La(III) oxides/hydroxides contributes to the enhanced corrosion resistance of the coatings by improving the adhesion of the conversion layer to the Galfan substrate and by facilitating the formation of a more uniform and compact layer. This uniformity and compactness significantly hinder the diffusion of corrosive agents through the coating, thereby protecting the metal substrate from corrosion.

2.2. Atomic force microscopy, AFM analysis

Figure 3 showcases Atomic Force Microscopy (AFM) images of Galfan specimens subjected to lanthanum salt passivation treatment for 10 seconds and 1 minute, respectively. The imagery elucidates the uneven surface topography of the lanthanum conversion coating, characterized by a pattern of raised peaks that resemble miniature mountains. Distinctly, the apexes on the samples processed for 10 seconds present as sharp, spire-like protrusions, whereas those on the 1-minute treated samples are wider and more elevated. Variations in the color intensity across the images indicate differences in height, with the coating's surface becoming increasingly undulated as the duration of the treatment extends. Roughness analysis data indicates that the average roughness (Ra) values for the 10-second and 1-minute treatments stand at 9.342 nanometers and 44.481 nanometers, respectively, and the root mean square roughness (Rq) values at 12.477 nanometers and 60.935 nanometers, respectively.

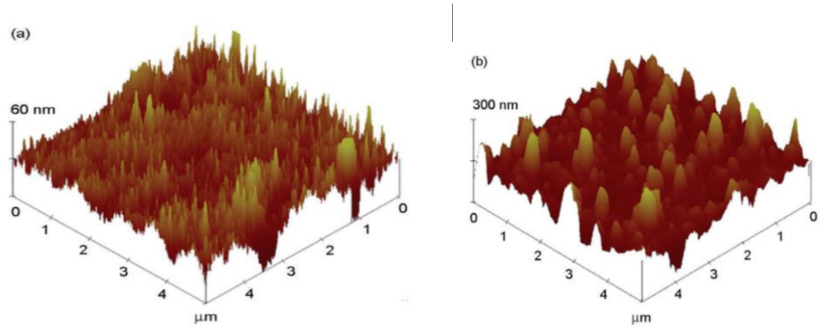

Figure 3. AFM diagram of lanthanum salt conversion film sample of Galfan coating.

2.3. Neutral Salt Spray Test, NSS analysis

Figure 4 illustrates the results of neutral salt spray (NSS) testing for samples of hot-dip galvanized Galfan and lanthanum conversion coatings subjected to different treatment durations. The NSS tests indicated that samples treated for 10 minutes showed substantially lower corrosion coverage compared to untreated samples and those treated for shorter or longer durations. This implies that the conversion film formed within this timeframe offers an optimal balance of coverage and protective properties. Electrochemical analysis, including polarization resistance and electrochemical impedance spectroscopy, further confirmed that the 10-minute treatment enhances the protective quality of the coating by reducing the corrosion current density and increasing the polarization resistance and impedance, indicative of a more resistive barrier against corrosion. This finding has significant implications for potential industrial applications, especially in transmission and transformation engineering, where materials are often exposed to harsh environmental conditions.

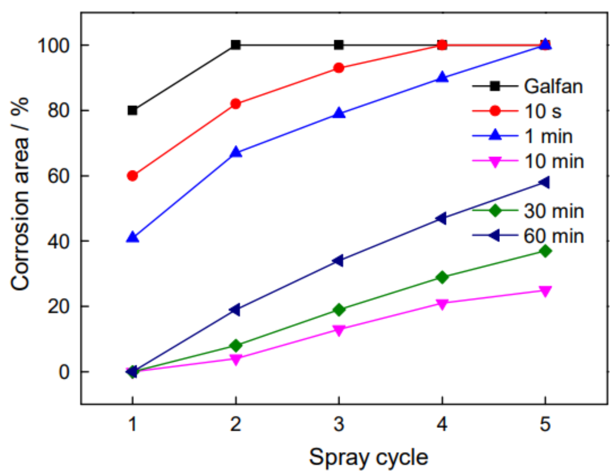

Figure 4. NSS results of Galfan and lanthanum salt conversion films were obtained at different treatment times.

3. Discussion

The hot-dip Galfan-coated samples were immersed in a lanthanum salt passivation solution containing NaF, where the solution, enriched with corrosive fluoride ions, accelerates the dissolution of the surface aluminum oxide layer under acidic conditions. This dissolution process contributes to the formation of a more uniform and dense conversion coating, thereby enhancing the corrosion resistance of the samples.

$$Al_2O_3 + F^- + H^+ \rightarrow AlF_3 + H_2O$$

Micro-anode area:

$$Zn - 2e \rightarrow Zn^{2+}$$

$$Al - 3e \rightarrow Al^{3+}$$

As H2O2 is added to the passivation solution, the following reactions will occur in the micro-cathode area

$$H_2O_2 + 2e \rightarrow 2OH^-$$

4. Conclusion

In transmission and transformation projects, the application of lanthanum conversion coatings on hot-dip Galfan coated surfaces results in superior corrosion resistance properties. Following a 10-minute treatment process, these lanthanum-based coatings markedly diminish the corrosion current density when compared to uncoated hot-dip Galfan counterparts, indicating a robust barrier against corrosion. Concurrently, there is a notable enhancement in both polarization resistance and electrochemical impedance, underscoring the coating's effectiveness in protecting the underlying metal. Consequently, a treatment duration of 10 minutes is identified as the optimal timeframe for achieving the most effective corrosion resistance, providing a significant improvement over untreated surfaces and contributing to the longevity and durability of infrastructure components in harsh environmental conditions. This finding underscores the potential of lanthanum conversion coatings as a viable and environmentally friendly alternative to traditional corrosion protection methods, offering new avenues for enhancing material performance in critical engineering applications.

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