

CORROSION RESISTANCE OF Cr(III) PASSIVATED ZINC ELECTRODEPOSITS

ĐỘ BỀN ĂN MÒN LỚP MẠ ĐIỆN KẼM THỤ ĐỘNG Cr(III)

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ABSTRACT

In this research, corrosion resistance of the Cr(III) passivated zinc electrodeposits was evaluated by the neutral salt spray test and electrochemical methods. The zinc electrodeposits were passivated in some different Cr(III) passive solutions, resulting in different colors of passive layers. The results of the neutral salt spray test showed that the iridescent Cr(III) passivated sample was the most corrosion resistant with 768 hours of testing for reaching 5% white rust area. These results agreed with those of the electrochemical methods that the iridescent Cr(III) passivated sample was also the most corrosion resistant with the lowest corrosion current density of $1.59\mu\text{A}/\text{cm}^2$ and the highest passive layer resistance of over $33.89\text{k}\Omega.\text{cm}^2$. The corrosion resistance of the passivated samples decreased in the order of the iridescent passivated samples, the white-blue passivated samples, the black passivated samples and finally the unpassivated samples.

Keywords: Zinc electrodeposit; corrosion; Cr(III) passivation.

TÓM TẮT

Trong nghiên cứu này, độ bền ăn mòn của các lớp mạ điện kẽm thụ động Cr(III) được đánh giá bằng thử nghiệm phun muối trung tính và các phương pháp điện hóa. Các lớp mạ điện kẽm được thụ động hóa trong một số dung dịch thụ động Cr(III) khác nhau, cho các lớp thụ động có màu sắc khác nhau. Kết quả thử nghiệm phun muối trung tính cho thấy mẫu thụ động Cr(III) cầu vồng có khả năng chống ăn mòn cao nhất với diện tích gỉ trắng đạt 5% sau 768 giờ thử nghiệm. Kết quả này phù hợp với kết quả của phương pháp điện hóa mà mẫu thụ động Cr(III) cầu vồng cũng có khả năng chống ăn mòn cao nhất với mật độ dòng ăn mòn thấp nhất là $1,59\mu\text{A}/\text{cm}^2$ và điện trở lớp thụ động cao nhất trên $33.89\text{k}\Omega.\text{cm}^2$. Độ bền ăn mòn của các mẫu thụ động giảm dần theo trật tự sau: mẫu thụ động cầu vồng, mẫu thụ động trắng xanh, mẫu thụ động đen và cuối cùng là mẫu kẽm không thụ động.

Từ khóa: Lớp mạ kẽm; ăn mòn; thụ động Cr(III).

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1. INTRODUCTION

The zinc electrodeposition is one of the most widely used methods to protect iron and steel structures because of its low cost and simple technology [1-2]. However, the zinc electrodeposit is corroded quite quickly in service life. Therefore, in order to improve the corrosion resistance of the zinc electrodeposit, various methods of surface treatment are researched and applied in practice [3, 4]. Among them, the most popular method is the chromate passivation. The formed passive film consists of a mixture of oxides and hydroxides of zinc and chromium, also their salts and complexes [3-5]. Depending on passive solutions, the thickness of passive films is different from hundred to thousand nano-meters [6, 7]. The disadvantage of this method is that the passive films contain highly toxic Cr(VI) ions which are hazardous for the humans and the environment. For that reason, many regulations have been introduced to restrict or prohibit the use of Cr(VI), but not applied to Cr(III) and metallic Cr [8, 9].

With the aim at replacing Cr(VI) passive solution, there have been many studies on Cr(III) passive solution in the world [5-10] and in Vietnam [11-13]. In the last 20 years, Cr(III) passive solutions have been used mainly in the production lines of automobile and motorcycle components and export goods in Vietnam. Using of Cr(III) passive solutions is an inevitable trend in environmental protection and towards cleaner production in Vietnam.

In this research, the zinc electrodeposits were passivated in different passive solutions, resulting passive films with different colors as white-blue, iridescent and black. The corrosion resistance of these Cr(III) passivated zinc electrodeposits was evaluated by salt spray acceleration test and electrochemical methods and the results were represented in this article.

2. RESEARCH METHODS

2.1. Preparation of experimental samples

The main chemicals used in the research including ZnCl_2 , NH_4Cl , KCl , H_3BO_3 , H_2SO_4 , HCl , HNO_3 were pure chemicals from China. In addition, the commercial

passivation solutions including Blue SSP, Kempas BZ 171 A, Kempas BZ 171 B, Zincovate TLP from India were also used.

The zinc electrodeposits were plated on carbon steel samples with dimension of 50 x 100mm. These steel samples were mechanically polished, degreased, and pickled. Then, the steel samples were activated in 5% v/v HCl solution for 5 seconds and plated in a bath with capacity of 25 liters. The solution composition and operating conditions were following:

Table 1. Composition of plating solution and operating conditions

Solution composition:		Operating conditions:	
ZnCl ₂	60g/L	pH	4.8 - 5.4
NH ₄ Cl	50g/L	Solution temperature	room temperature
KCl	200g/L	Cathodic current density	2A/dm ²
H ₃ BO ₃	20g/L	Plating time	30 minutes
Zincobrite AZ Carrier	30mL/L		
Zincobrite AZ Brighter	1mL/L		

Before passivated, the zinc electrodeposits were activated in 0.5% v/v HNO₃ solution for 5 seconds. Then, these zinc electrodeposits were shaken in different Cr(III) passive solutions with different passivating times. The Cr(III) passive solutions and operating conditions were following:

Table 2. Passivating solutions and operating conditions

Solutions		pH	Passivating time	Color of passive films
Blue SSP	100mL/L	2.0 - 2.8	50s	white-blue
Kempas BZ 171 A	50mL/L	3.8 - 5.5	40s	black
Kempas BZ 171 B	50mL/L			
Zincovate TLP	100mL/L	1.4 - 3.4	40 s	iridescent

pH of the passive solutions was measured with a pH meter Milwaukee MW101 and adjusted with solutions of HNO₃ or NH₄OH. After passivated, the samples were washed with water, dried with a blower and then in an oven at 80°C for 30 minutes.

2.2. Experimental techniques

Salt spray acceleration test

Table 3. Salt spray test conditions for neutral salt spray test (JIS H 8502 : 1999)

Concentration of NaCl, g/l	pH of solution	Amount of spray, ml/80 cm ² /hour	Temperature in test vessel, °C	Temperature in air saturator, °C	Pressure of compressed air, kPa
50 ± 5	6.5 - 7.2	1.5 ± 0.5	35 ± 2	47 ± 2	70 - 167

The purpose of the salt spray test is to compare the corrosion resistance of samples in the same test or to assess the difference between the testing specimen and the previously tested sample. Neutral salt spray test according to JIS H 8502:1999 standard was used to evaluate these Cr(III) passivated zinc electrodeposits. Equipment used in

this research was Q-FOG CCT 600 (USA) at Institute for Tropical Technology.

Electrochemical methods

To determine corrosion resistance of the samples, an electrochemical cell of three electrodes including platinum electrode, saturated calomel electrode and the sample with electrolyte as 3.5% NaCl solution was used. Electrochemical measurements were conducted by equipment of Biologic VSP-300 at Institute for Tropical Technology.

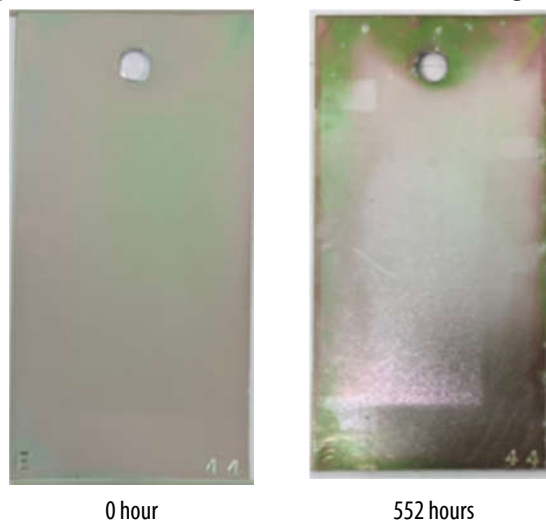
Tafel polarization curve. The polarization curves of the Cr(III) passivated zinc electrodeposits were measured according to Tafel method to determine i_{corr} . The potential steps were scanned from $E_{corr} - 200mV$ to $E_{corr} + 200mV$ with scan rate of 1mV/s at a temperature of 25°C. The plots in the form of points represented the relationship between E and i. From these plots, i_{corr} of the Cr(III) passivated zinc electrodeposits was determined by extrapolating the polarization curve (E - lgi) at E_{corr} .

Electrochemical impedance spectroscopy. The electrochemical impedance spectroscopies of the Cr(III) passivated zinc electrodeposits were performed in conditions with AC voltage amplitude of 10mV at E_{corr} and frequency range from 10kHz to 10mHz. Area of the samples for electrochemical methods was 4.52cm².

3. RESEARCH RESULTS AND DISCUSSION

3.1. Salt spray acceleration test

The iridescent Cr(III) passivated samples. Figure 1 shows images of the iridescent Cr(III) passivated samples at different periods in neutral salt spray test. After 168 hours of salt spray, the surfaces of the iridescent passivated samples were still shiny, bright and not any changes. After 552 hours, white rust spots started to appear on the surfaces and areas with white rust reached about 5% after 768 hours. After 1000 hours of salt spray, the surface areas of the iridescent passivated samples covered by white rust were 25 - 35% and no red rust spots appeared. Therefore, it could be estimated that the iridescent Cr(III) passivated samples were stable more than 700 hours of testing.



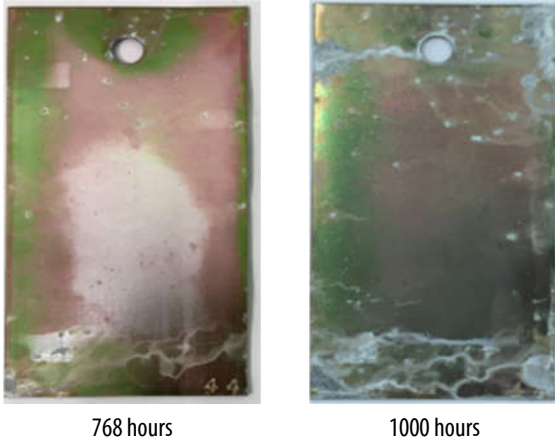


Figure 1. Images of the iridescent Cr(III) passivated samples at different periods

The white-blue Cr(III) passivated samples. After 24 hours of neutral salt spray, the surfaces of the white-blue passivated samples had stains that could see on Figure 2. White rust spots started to appear on the surfaces after 48 hours, and after 72 hours of salt spray, surface areas with white rust expanded about 5%. After 888 hours of salt spray, red rust spots started to appear on the surfaces. After 1000 hours of salt spray, the surfaces of the white-blue passivated samples covered red rust were about 5%.

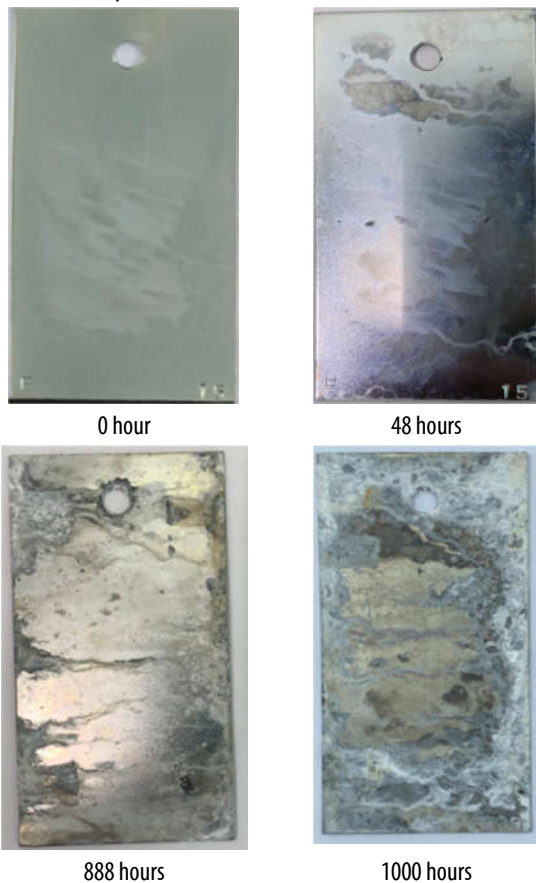


Figure 2. Images of the white-blue Cr(III) passivated samples at different periods

The black Cr(III) passivated samples. Figure 3 shows images of the black Cr(III) passivated samples at different

periods. After 24 hours of neutral salt spray test, 80% of the surfaces of the black passivated samples were covered by white rust. After another 24 hours, white rust covered the entire surface of the samples. Red rust spots started to appear on the surfaces after 216 hours of salt spray. After 1000 hours of salt spray, the surfaces of the black passivated samples covered red rust were about 85%.

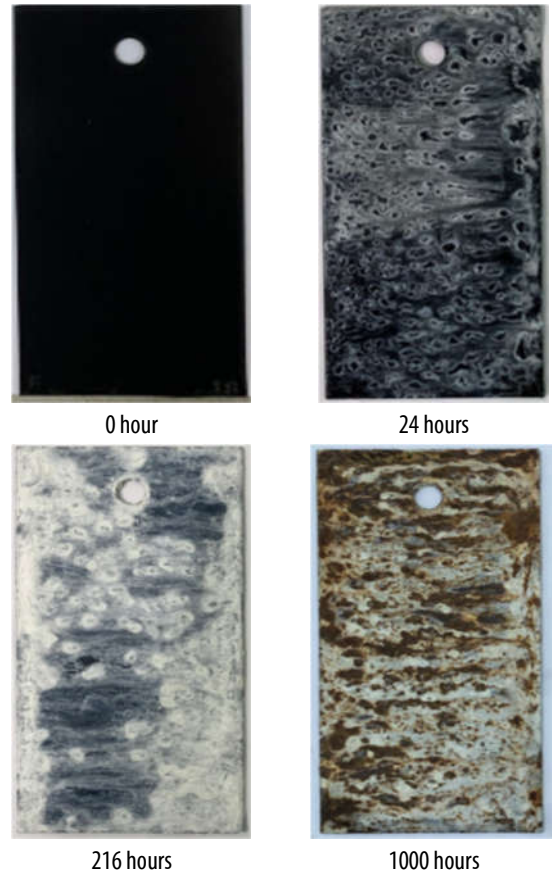


Figure 3. Images of the black Cr(III) passivated samples at different periods

The unpassivated zinc electrodeposits. After 24 hours of neutral salt spray test, the entire surfaces of the zinc electrodeposits were covered by white rust. After 96 hours of salt spray, red rust spots started to appear on the surfaces of samples. At the end of test, the surfaces of the unpassivated zinc electrodeposits covered red rust were about 95%.



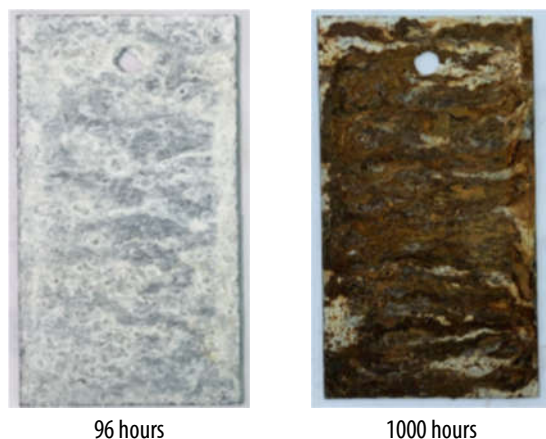


Figure 4. Images of the unpassivated zinc electrodeposits at different periods

Table 4. Main periods of the samples in the neutral salt spray test

	unpassivated zinc samples	black passivated samples	white-blue passivated samples	iridescent passivated samples
White rust appeared	~ 1h	~ 4h	48h	552h
5% white rust	~ 3h	~ 7h	72h	768h
Red rust appeared	96h	216h	888h	> 1000h

The important periods for evaluating the corrosion resistance of the Cr(III) passivated zinc electrodeposits in the neutral salt spray test were summarized in Table 4. From the data in the table, it could be easy to see that the iridescent Cr(III) passivated samples were the most corrosion resistant with 768 hours of testing for reaching 5% white rust area and over 1000 hours for appearing red rust spots. The corrosion resistance of the Cr(III) passivated zinc electrodeposits decreased in the order of the iridescent passivated samples, the white-blue passivated samples, the black passivated samples and finally the unpassivated samples.

3.2. Electrochemical methods

Tafel polarization curve. The polarization curves of the Cr(III) passivated zinc electrodeposits and the electrochemical parameters calculated from these curves were represented in Figure 5 and Table 5. The data in the table show that the iridescent Cr(III) passivated sample with lowest corrosion current density of $1.59\mu\text{A}/\text{cm}^2$ was the most corrosion resistant. Corrosion resistance of the passivated samples decreased in the order of the iridescent sample, the white-blue sample, the black sample and finally the unpassivated zinc sample with highest corrosion current density of $14.57\mu\text{A}/\text{cm}^2$, that agreed with results of the neutral salt spray test.

Note: in figures and tables, the passivated samples were marked as following Zn for unpassivated zinc sample, Zn/Cr3CV for iridescent passivated sample, Zn/Cr3TX for white-blue passivated sample, and Zn/Cr3D for black passivated sample.

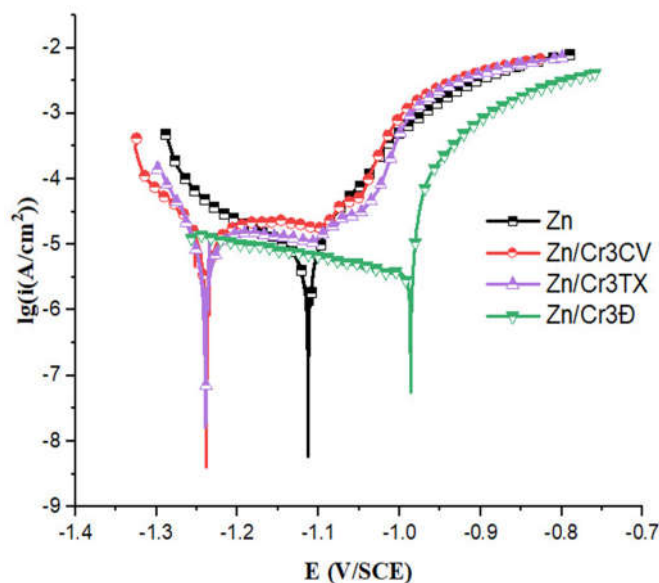


Figure 5. Tafel polarization curves of the Cr(III) passivated samples

Table 5. The electrochemical parameters calculated from the polarization curves

Sample	β_a (mV/decade)	β_c (mV/decade)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV vs SCE)
Zn	83.6	349.7	14.57	-1113
Zn/Cr3CV	120.5	39.3	1.59	-1239
Zn/Cr3TX	236.6	43.2	4.65	-1232
Zn/Cr3D	124.8	436.1	8.30	-989

Electrochemical impedance spectroscopy.

To understand more clearly the corrosion resistance of the Cr(III) passivated zinc electrodeposits, electrochemical impedance spectroscopy of these samples was investigated. Figure 6 and Table 6 show EIS spectra of the Cr(III) passivated samples and the electrochemical parameters fitted from these spectra. As could be seen in Figure 6, the Nyquist plot of the iridescent passivated sample existed a diffusion line which showed that the passive layer had not been broken. The passive layer resistance of the iridescent passivated sample was also the highest, over $33.89\text{k}\Omega.\text{cm}^2$. Meanwhile, the Nyquist plots of the white-blue and black passivated samples both appeared two semicircles, indicating that the passive layer of these samples has been damaged. The passive layer resistance and charge transfer resistance of the white-blue passivated sample are higher than the respective resistances of the black passivated sample. For the unpassivated zinc sample, the charge transfer resistance of $0.87\text{k}\Omega.\text{cm}^2$ was much smaller than that of the passivated samples. Thus, it could be confirmed that the iridescent passivated sample was the most corrosion resistance, followed by the white-blue passivated sample, the black passivated sample and finally the unpassivated zinc sample.

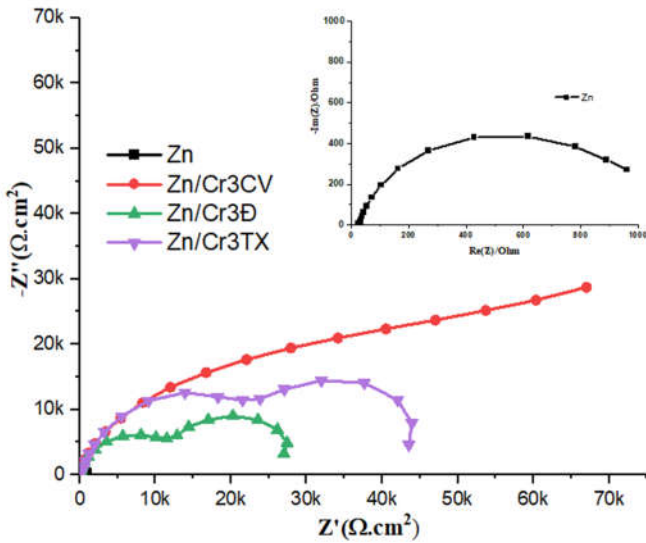


Figure 6. EIS spectra of the Cr(III) passivated samples

Table 6. The electrochemical parameters calculated from the EIS spectra

Sample	R_s ($\Omega.cm^2$)	R_{pi} ($k\Omega.cm^2$)	C_{pl} ($\mu F/cm^2$)	C_{dl} ($\mu F/cm^2$)	R_{ct} ($k\Omega.cm^2$)
Zn	27.50	-	-	13.4	0.87
Zn/Cr3CV	27.09	33.86	5.69	-	-
Zn/Cr3TX	27.63	21.64	0.38	1.22	31.42
Zn/Cr3Đ	29.39	10.94	5.42	97.1	16.72

4. CONCLUSION

From the results of the neutral salt spray test and electrochemical methods, it could be concluded that the iridescent Cr(III) passivated samples were the most corrosion resistance, followed by the white-blue Cr(III) passivated samples, and then the black Cr(III) passivated samples. These Cr(III) passivated samples are all more corrosion resistant than unpassivated zinc electrodeposits.

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