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THE EFFECTS OF DRYING TEMPERATURE ON THE STRUCTURE AND CORROSION RESISTANCE OF Cr^{3+}-BASED CONVERSION COATINGS ON ZINC-COATED STEEL SURFACE

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ABSTRACT

In this paper, we present results of drying temperature influence on the structure and corrosion resistance of Cr(III)–based conversion coatings on the surface of zinc-coated steel. The results show that the quality of Cr(III)–based conversion coatings is strongly influenced by the drying temperature, the appropriate drying temperature is about 80 °C, and drying at higher temperatures will reduce corrosion resistance durability and raise the cost of the production process.

Keywords: Cr(III)–based conversion coatings, zinc, SEM, corrosion, polarization, conversion.

1. INTRODUCTION

Zinc coatings are widely used to protect steel details and components in different industries. However, the zinc coating layer can be rapidly corroded in moist air. Therefore, to improve the resistance of zinc coatings against corrosion, various methods of surface treatment are used, among which the most common one is the use of the conversion chromate layer [1, 2]. The conversion chromate layer has many advantages: high corrosion resistance, reparation convenience, color diversity (white, rainbow, black, olive), good adhesion for organic coatings, simplified technology, low cost, etc.. [3]. The thickness of the conversion layers ranges from 100 to 1500 nm, depending on its color [4]. However, solutions and conversion layers containing Cr^{6+} ion are highly toxic and potentially carcinogenic and require high costs of wastewater treatment. Cr^{6+} proportion in the conversion layer ranges from 5 to 400 mg/m^2 [4, 5], and in the process of being used it will gradually dissolve, polluting the environment.

To replace the conversion layer Cr^{6+}, many other passive solutions are considered, in which the solution containing Cr^{3+} ion is mostly studied and has been used in making some industrial products that are accepted by automakers in the world [6, 7].

With the aim of systematically studying and testing the conversion layer Cr^{3+} manufactured at Institute of Tropical Technology, improving conversion solutions to use them in production, in this paper we present the results of studying the effects of drying temperature on the structure and corrosion resistance of Cr(III)–based conversion coatings on zinc-coated steel surface.

2. EXPERIMENT

2.1. Creating prototype

Samples for experiment: Carbon steel pieces of 100×50×1.2 mm size were polished by emery paper, degreased, pickled and then galvanized (according to ENTHONE company's ULTIMAT AZ) in a bath of 25-litre capacity volume with its composition and galvanizing modes as shown in Table 1.

Table 1. Composition and galvanizing mode.

$ZnCl_2$	60 g/l	NH_4Cl	250 g/l
AZA	30 ml/l	AZB	1.5 ml/l
pH	4.8 - 5.4	Temperature	Normal
D_k	2A/dm^2	Time	30 minutes
Anode	Zinc 99.995 %	Mixing Mode	Swaying cathode

The zinc coating layer achieved the average thickness of 13 micrometers.

Converting the zinc coatings: Zinc-coated samples were activated in HNO_3 solution of 0.5 % concentrationin 3 - 5s. The samples conversion was performed for one by one with 2 different solutions: C solution is a Cr(III) rainbow solution produced at Institute of Tropical Technology, SP25 solution is a Cr(III) industrial solution of SpectraMATETM 25 (Columbia).

Table 2. The basic components of conversion solution C.

Cr(III) (as $Cr_2(SO_4)_3$. $6H_2O$)	5 g/l
Chelating	6 g/l
Co(II) (as $CoSO_4.7H_2O$)	2 g/l
CH_3COOH	10 ml/l
pH	2.0 - 2.5
Time embedded	60s
Temperature	20 - 30 °C

Table 3. Parameters of conversion solution SpectraMATE 25.

Parameters of the conversion solution	Optimal
SpectraMATE^{TM}25	100ml/l
Temperature	20 - 30 °C
Time Embedded	60s
pH	2.0 - 2.5

The pH was measured by pH METERLAB pHM210 and adjusted by HNO_3 or NH_4OH.

After conversion, the samples were washed with water, distilled water, blown and dried at 4 different temperatures (50 °C, 80 °C, 110 °C and 210 °C) for 30 minutes.

2.2. Testing methods

Conversion coatings, after having been dried at different temperatures, are put in normal conditions for 48 hours, and their color are then evaluated by human eyes.

To determine the mass of zinc-coatings, the mass of the conversion coatings, weight loss after drying, the samples' weights are measured by SHIMADZU AEG-220 g weight analyzing balance with 0.0001g precision:

m_o - the mass of the steel sample before galvanization,

m_1 - the mass of the sample after galvanization,

m_2 - the mass of the sample after conversion,

m_3 -the mass of the sample after peeling the conversion coatings,

m_4 - the mass of the conversion sample after drying at different temperatures.

Corrosion resistance durability of the conversion coatings was determined by the method of salt spraying (NSS) according to JIS H 8502:1999 standard in salt blind cabinet Q-FOG CCT 600 (US) at Institute of Tropical Technology.

The morphology of the conversion coatings was studied by scanning electron microscope (SEM) HITACHI S-4800.

Corrosion behavior of conversion zinc coatings was determined by the polarized static method with the device AUTOLAB PGSTAT 30 with three electrodes: the sample with 4.52 cm^2 square, the platinum electrode, the comparative calomen electrode saturated in NaCl 3.5 % with natural ventilation. Scanning speed was 2 mV/s.

3. RESULTS AND DISCUSSION

3.1. Loss of conversion layer mass by drying

The weight loss and the weight loss ratio of the conversion layer after having been dried at different temperatures are presented in Table 4, Figure 1 and Figure 2.

Table 4. Weight loss of the conversion layer after having been dried.

Solution	Drying temperature	Sample	m_2(g)	m_4(g)	Δm(mg) $(m_2 - m_4).1000$	$\Delta\overline{m}2$ (mg)	$\frac{\Delta \overline{m}\ 2}{\Delta \overline{m}\ 1}.100$
Sp25	50 °C	1	40.9488	40.9475	1.3	1.27	1.21 %
		2	40.4197	40.4184	1.3		
		3	40.8818	40.8806	1.2		
	80 °C	1	40.9418	40.9403	1.5	1.47	12.97 %
		2	40.4573	40.4558	1.5		

Solution	Drying temperature	Sample	m_2(g)	m_4(g)	Δm(mg) (m_2 -m_4).1000	$\Delta\overline{m}2$ (mg)	$\frac{\overline{\Delta m\ 2}}{\Delta m\ 1}$.100
		3	40.4954	40.4940	1.4		
	110 °C	1	40.9921	40.9899	2.2	2.13	18.8 %
		2	40.8336	40.7315	2.1		
		3	40.5705	40.5684	2.1		
	210 °C	1	40.3462	40.3432	3	2.9	25.6 %
		2	40.6333	40.6305	2.8		
		3	40.7772	4.7743	2.9		
C	50 °C	1	40.6209	40.6198	1.1	1	8.59 %
		2	40.6027	40.6018	0.9		
		3	40.474	40.473	1		
	80 °C	1	40.2034	40.2022	1.2	1.33	11.4 %
		2	40.3057	40.3043	1.4		
		3	40.1547	40.1533	1.4		
	110 °C	1	40.4702	40.4682	2	2	17.14 %
		2	40.4479	40.4458	2.1		
		3	40.5261	40.5242	1.9		
	210 °C	1	40.9072	40.9043	2.9	2.83	24.34 %
		2	40.1705	40.1677	2.8		
		3	40.5959	40.5931	2.8		

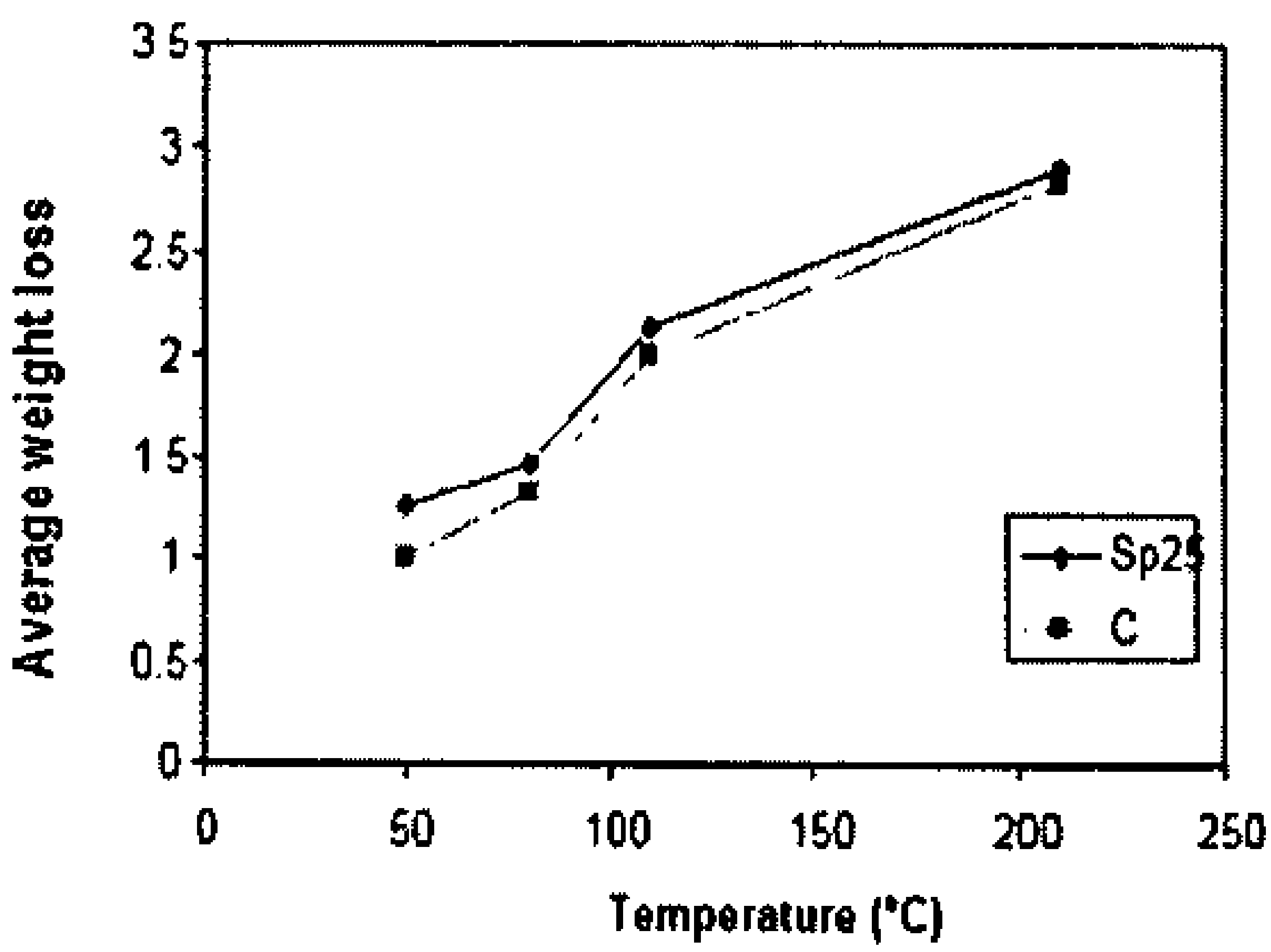


Figure 1. Weight loss of the conversion layer in drying at different temperatures.

From the results on Table 4, Figure 1 and Figure 2, it can be seen that the loss of mass after drying in the conversion layer received from different solutions increases as the temperature increases from the normal temperature up to 210 °C. However, weight loss by drying does not increase linearly, the layer's mass decreases rapidly along the increase in drying temperature from the normal temperature up to 110 °C, then decreases slowly when the temperature increases from 110 °C to 210 °C (Figure 1). Changes in the mass of the conversion layer by drying, as we think, are mainly due to the loss of crystallized water in it. At the same drying temperature, mass loss does not differ much in the two kinds of conversion layer in research.

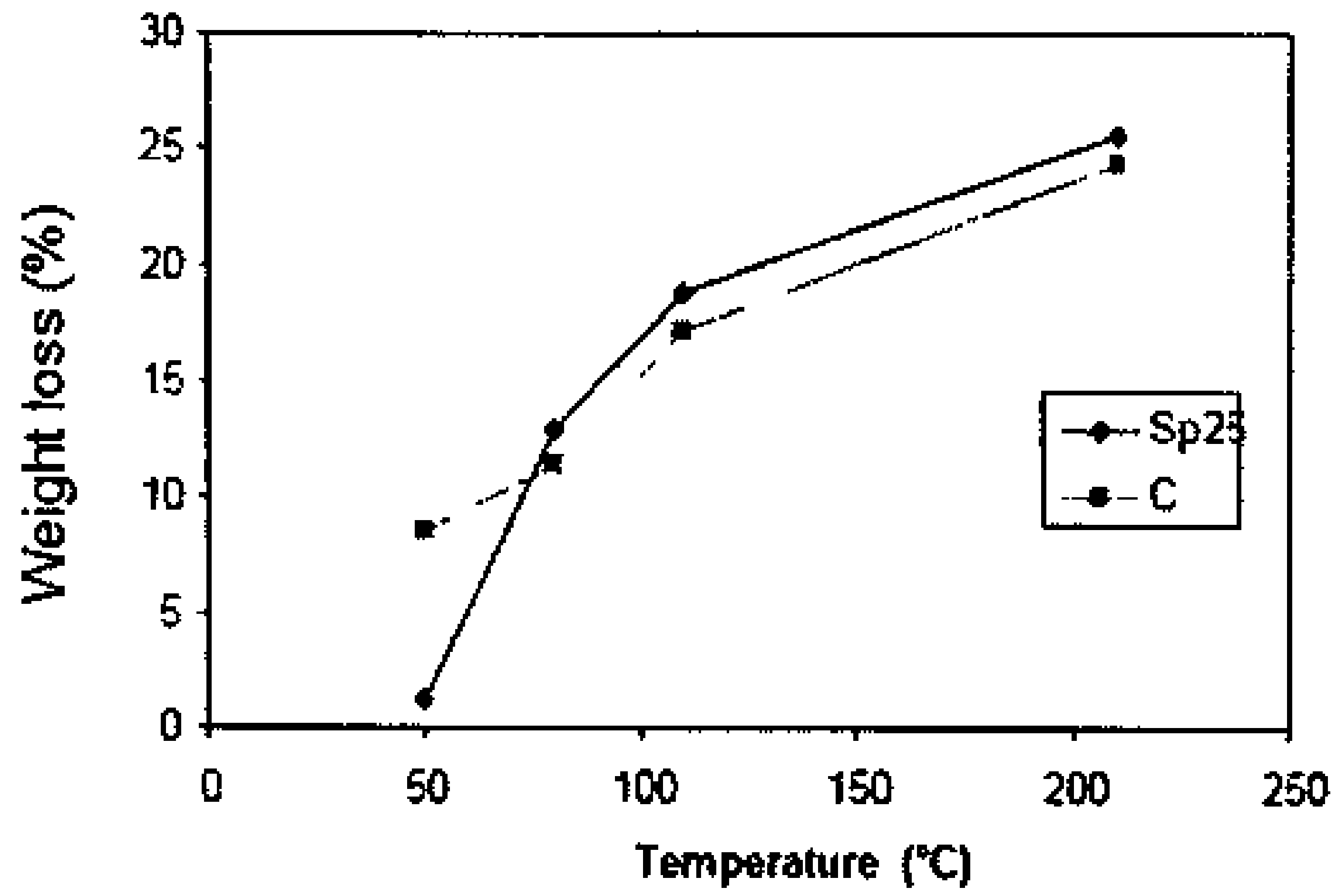


Figure 2. Percentage of weight loss (%) of the conversion layer in drying at different temperatures.

3.2. Salt-blind tests

The average duration of salt spraying (white rust surface appearance) of the conversion layer is presented in Table 5.

Table 5. Corrosion resistance durability of various kinds of conversion layer.

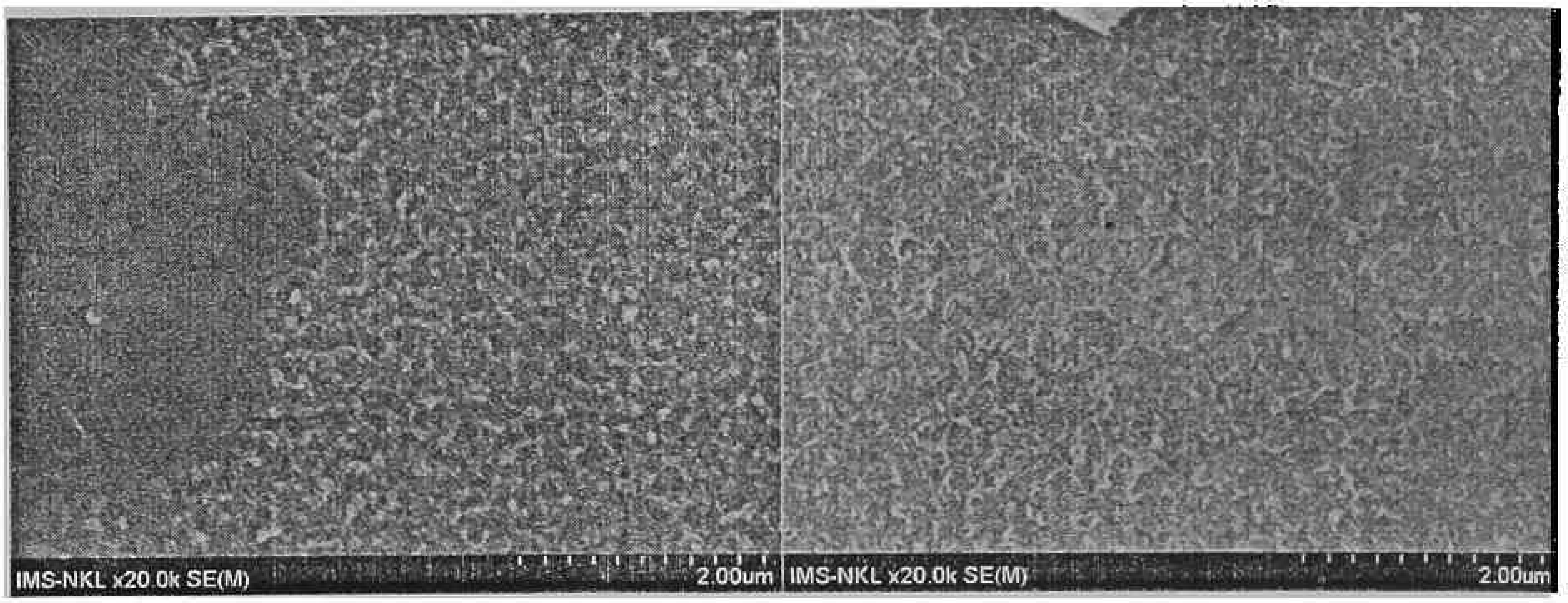
T^0 / conversion layer	Time of white surface rust appearance, hour			
	50 °C	80 °C	110 °C	210 °C
C	194	218	195	175
SP25	175	220	190	160

The salt spraying results in Table 5 shows: The samples done with C and SP25 offer the same results that those samples experiencing the drying temperature of 210 °C have the worst corrosion resistance durability. Salt spraying durability of the samples can be arranged as follows: 50 °C < 80 °C > 110 °C > 210 °C.

At the drying temperature of 80 °C the samples of Cr^{3+}-based conversion coatings achieve the maximum salt spraying time.

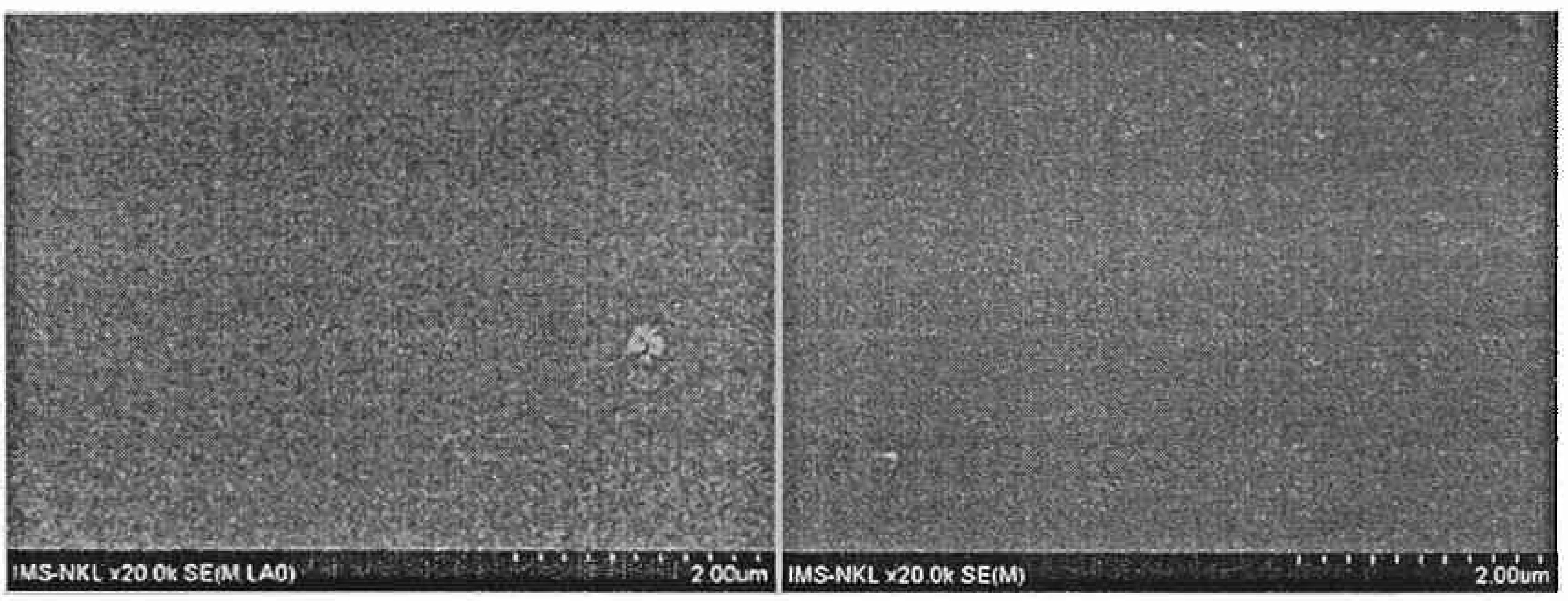
3.3. Morphology of the Cr^{3+}-based conversion coatings

Morphology of the Cr^{3+}-based conversion coating is shown in Figure 3 and Figure 4. Here we offer images of the the Cr^{3+}-based conversion coating at the optimal drying temperature (according to the salt-blind tests) and at the drying heat of 210 °C.



a) 80 °C b) 210 °C

Figure 3. Morphology of the galvanized conversion layer with the solution SP25.



a) 80 °C b) 210 °C

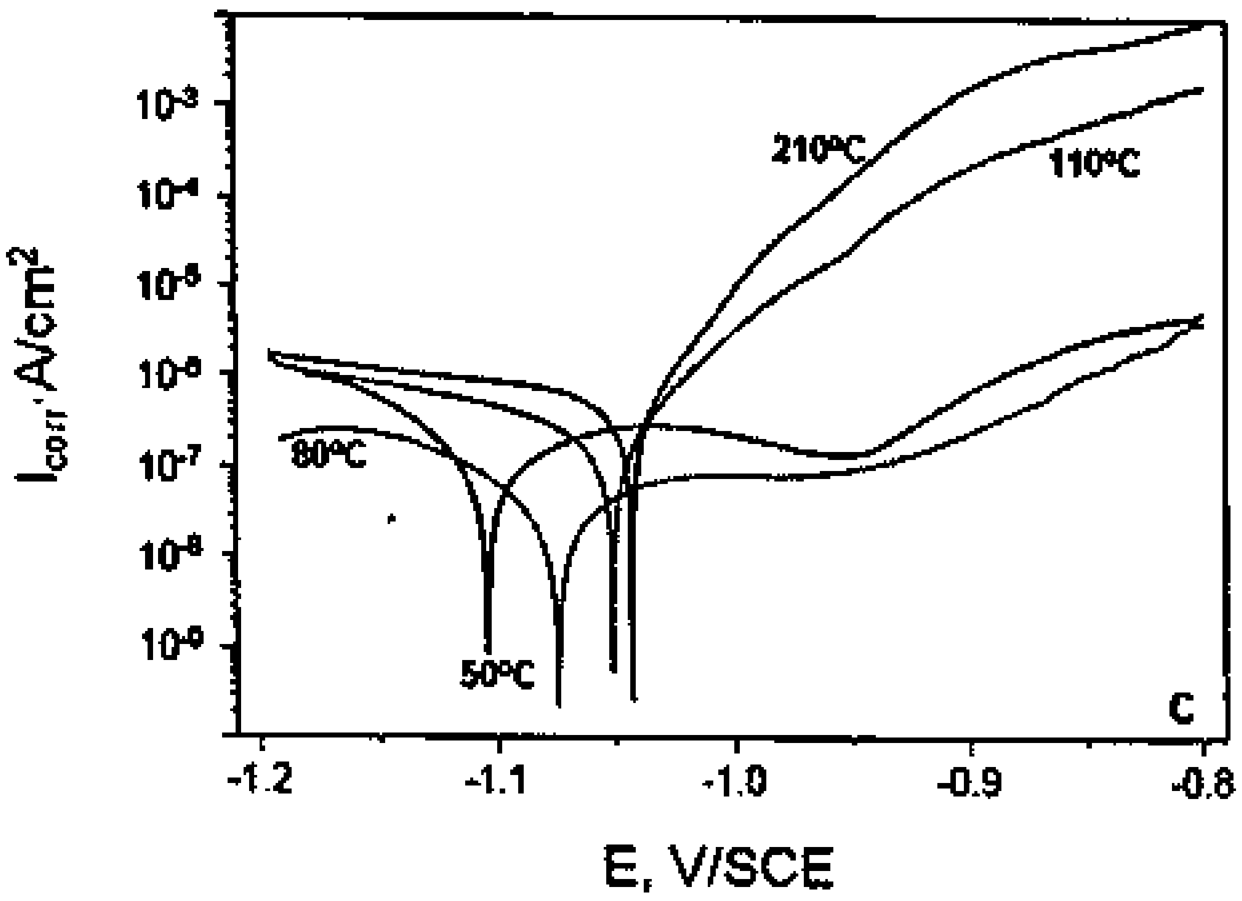
Figure 4. Morphology of the galvanized conversion layer with the solution C.

From Figure 3 and Figure 4, it is seen that the surface of all the samples is smooth, small particles are evenly distributed over the surface. At the drying temperatures of 80 °C and 210 °C, the surface passive layer has completely no fracture crack.

3.4. Polarization measurement results

The dynamic polarization curves of the samples of passive layer heated at different temperatures are shown in Figure 5 and Figure 6. The electrical potential value and the corrosion current density are shown in Table 6.

The corrosion current density of the samples is determined by Tafel extrapolation method on the two branches of the polarization curve.



Hình 5. Polarization curve of the sample of C.

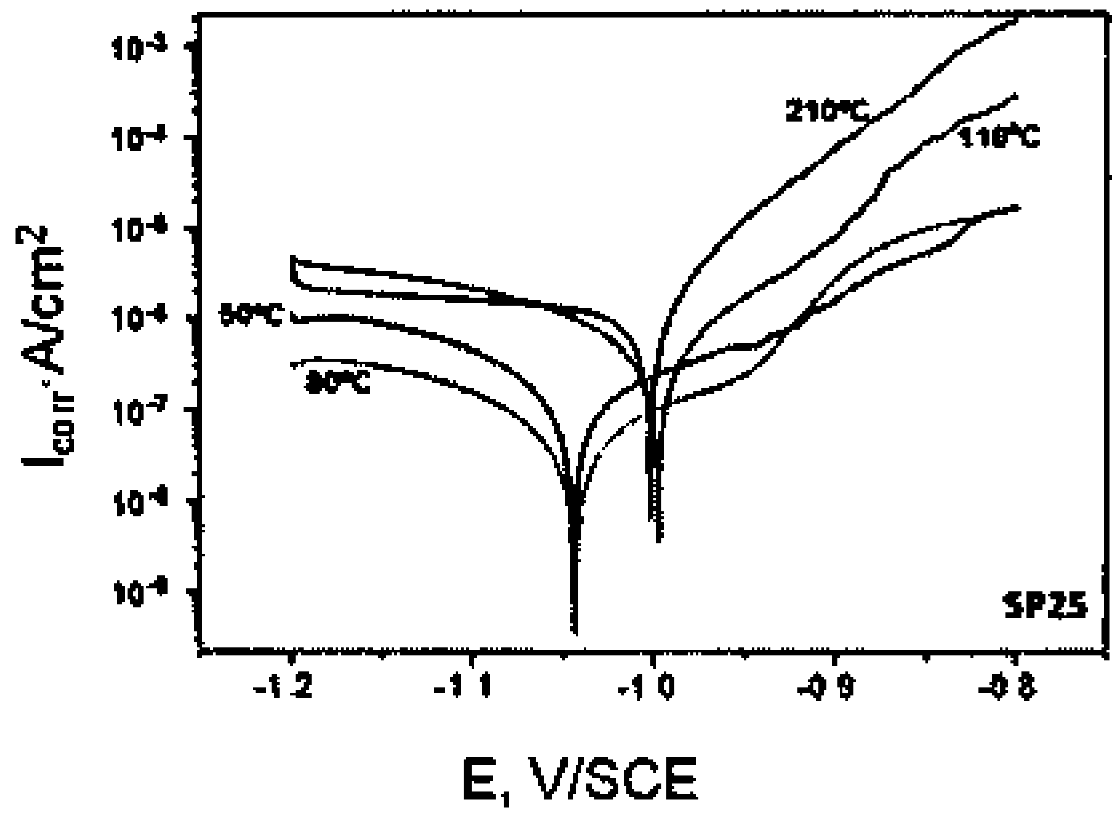


Figure 6. Polarization curve of the sample of SP25.

From Figure 5, 6 and Table 6, we can see:

- Corrosion potentials of the passive layer at the drying temperature 50 °C and 80 °C are more negative than those at the drying temperature 210 °C and 110 °C.

- The value of corrosion current density of the conversion layer decreases respectively with the drying temperature 210 °C, 110 °C, 50 °C and 80 °C. This result is consistent with the blind salt experimental results (Table 5). Corrosion durability of the prototype samples: 50 °C ~ 80 °C > 110 °C > 210 °C.

Table 6. Values of E_{corr} and i_{corr} of passive layer Cr(III).

Solution	Drying temperature (^{0}C)	E_{corr}, mV/SCE	i_{corr}, A/cm^2
C	210	-1046	5.87×10^{-7}
	110	-1053	1.52×10^{-7}
	80	-1074	3.35×10^{-8}
	50	-1104	6.6×10^{-8}
Sp25	210	-1004	8.94×10^{-7}
	110	-996	4.62×10^{-7}
	80	-1044	2.67×10^{-8}
	50	-1045	8.55×10^{-8}

4. CONCLUSIONS

When drying the conversion layer of Cr(III) at different temperatures, we can see:

- The smoothness of the sample surface is not affected, the conversion layer is not peeled.

- The mass of the conversion layer decreases around 8.6 to 17.14 % while increasing the drying temperature from 50 to 110 °C.

- When increasing the temperature of drying the conversion layer, corrosion resistance durability reaches optimum at about 80 °C, then decreases as the temperature continues to rise.

Through the above analysis, the appropriate temperature of drying conversion layer is about 80 °C, drying at higher temperatures will reduce corrosion resistance durability, further add to the cost of production process.

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TÓM TẮT

ẢNH HƯỞNG CỦA NHIỆT ĐỘ SẤY ĐẾN CẤU TRÚC VÀ ĐỘ BỀN CHỐNG ĂN MÒN CỦA LỚP THỤ ĐỘNG Cr^{3+} TRÊN BỀ MẶT THÉP MẠ KẼM

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Trong bài báo này, chúng tôi trình bày kết quả nghiên cứu ảnh hưởng của nhiệt độ sấy đến cấu trúc và khả năng chống ăn mòn của lớp thụ động Cr (III) trên bề mặt của thép mạ kẽm. Kết quả cho thấy nhiệt độ sấy ảnh hưởng rất lớn đến chất lượng của lớp thụ động Cr (III), nhiệt độ sấy thích hợp là khoảng 80 °C, ở nhiệt độ cao sẽ làm giảm độ bền ăn mòn của lớp thụ động và làm tăng chi phí của quá trình sản xuất.

Từ khóa: lớp thụ động Cr(III), kẽm, SEM, ăn mòn, phân cực.