

CHARACTERIZATION OF DARK GREEN PASSIVATION FILM ON GALVANIZED STEEL SHEET

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Abstract. Galvanized Steel Sheet was dark green colored passivated in tetracid solution system with acetic acid solution as stabilizer and silver salt solution as toner. The micro-morphology of the film before and after passivation was observed by SEM. The composition of the film was tested by EDS and its phase composition was analyzed by XRD. The corrosion resistance of the passivated film was studied by neutral salt spray test. The results showed that the surface of the specimen without passivation film was complete consecutive and coarse electrodeposited zinc coating. The surface became homogeneous and smooth, and turned dark green with the uniform colour and soft brightness but had chap structure. The film was composed of Cr, O, P, Zn, and a small amount of Fe element. There were phases in the film, including CrPO_4 , $\text{Cr}(\text{OH})_3$, CrOOH , Cr_2O_3 , $\text{Zn}(\text{OH})_2$, $2\text{ZnORCrO}_3\text{RH}_2\text{O}$, $\text{Zn}_3(\text{PO}_4)_2\text{R}_4\text{H}_2\text{O}$, and Ag. Zinc coating, passivation film, and Fe matrix combined closely, and no defects appeared such as crack. The total thickness of zinc coating and passivation film reaches $12.423\ \mu\text{m}$, and dark green passivation film is $1.734\ \mu\text{m}$. The passivation film could endure neutral salt spray test for 400 h, which met the demands of national and enterprise standards.

1. INTRODUCTION

The blackishgreen passivation handicraft we designed just has good compatibility with the potassium chloride zinc plating handicraft one of the green environmental protection electroplating produces handicraft. The appearance of galvanized sample treated by this passivation craft was blackishgreen, colour was uniform and lustre was gentle. The passivation film can endure neutral salt spray test for 400 h. The passive film were characterized in this paper to determine its microstructure, phase composition and corrosion resistance.

2. EXPERIMENTAL

2.1. Pretreatment and preparation of substrate

No. 20 high quality carbon structural steel samples were machined into rectangular blocks with $20 \times 20 \times 2$

mm^3 in size. Its superficial electroplated layer is prepared by potassium chloride zinc plating handicraft. The solution of the mixture ($210 \sim 240$) $\text{g} \cdot \text{L}^{-1}$ KCl + ($55 \sim 75$) $\text{g} \cdot \text{L}^{-1}$ ZnCl + ($25 \sim 30$) $\text{g} \cdot \text{L}^{-1}$ H_3BO_3 + ($12 \sim 18$) $\text{mL} \cdot \text{L}^{-1}$ KZ-2000 Brightener was selected as potassium chloride zinc plating solution. The matrix was put into electrogalvanizing solution at ($5 \sim 50$) $^\circ\text{C}$ after degreasing and activating. The solution pH was dominated by precise pH indicator paper to 5.4~6.2. Current density was controled in the range of 0.5 to $3.5\text{A} \cdot \text{dm}^{-2}$ by rectifier. The thickness of galvanized coating was determined by TT210 coating thickness gauge no less than $15\ \mu\text{m}$.

Chemical pure reagents were used in passivation solution. The formulation of blackishgreen passivation agent was 30 g/L CrO_3 + 11 ml/L H_3PO_4 + 6 ml/L H_2SO_4 + 4 ml/L HNO_3 + 4 ml/L stabilizer (The main component was acetic acid) + 10 ml/L toner (Silver salt solution) was selected as blackishgreen passivation agent. The pH of blackishgreen passi-

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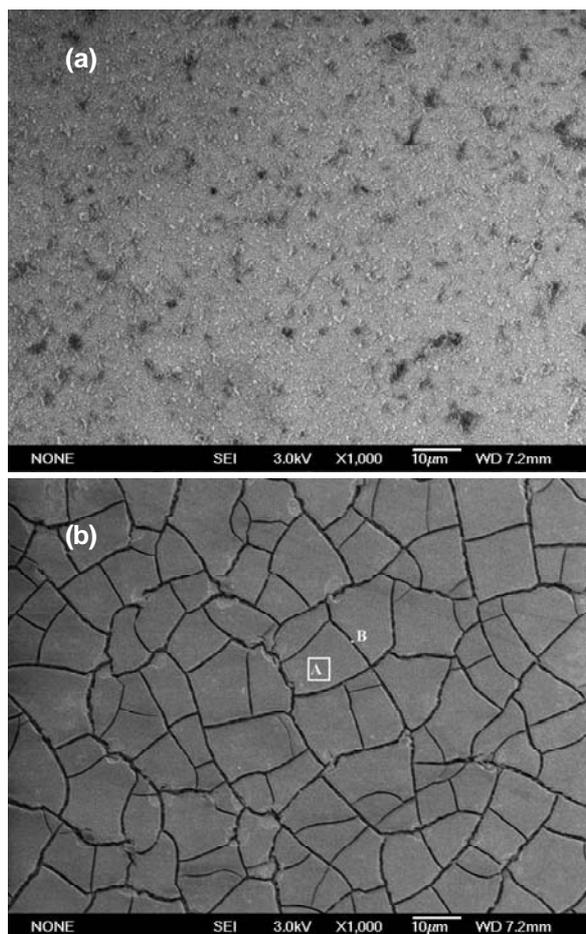


Fig. 1. Surface morphology of the specimens with and without blackishgreen colored passivation film: (a) Specimen without passivation film; (b) Specimen with blackishgreen colored passivation film.

vation agent was adjusted in the range of 1.0 to 1.5 by acetic acid [1,2].

After the galvanized sample was washed twice, its surface light extraction was conducted in 1% volume fraction of nitric acid, then it was washed by clear water and deionized water in turn. Second, the galvanized sample was suspended motionless in air for (60~120) s after it had been jittered slightly in passivation solution tempering (20~30) °C for (35~60) s, then it was absterged by deionized water. Finally, the blackishgreen passivation samples were prepared successfully by isothermally dried at 57 °C for 15 min or atmospheric dried.

2.1. Test method

During research of the blackishgreen colored passivation films, the Surface morphologies of coatings were identified by JSM-6700F field emission scanning electron microscopy (FESEM) under the test condition of accelerating voltage 3.0 kV, the

fracture surface morphology of coatings were identified by QUANTA200 environmental scanning electron microscope (ESEM). Elements of passivation film were confirmed by using X-ray energy dispersion spectrometer (EDS) through microdiffraction, line and surface scanning under the test condition of accelerating voltage 25 kV and emergence angle 35 degree. The phase composition was studied by X-ray diffraction analysis (XRD) under the test condition of grazing angle 0.0625 degree, copper target ($\text{Cu-K}\alpha$), pipe pressure 40 kV, pipe flow 35 mA, scanning speed 3 degree per minute, and sample scanning range from 30 to 90 degree. To evaluate the corrosion protection of the blackish green passivation films on zinc-plated steel sheet, according to GB/T6458-1986 (neutral salt spray, NSS), 5% NaCl was atomized in a salt spray chamber at 35 °C with a solution of pH approximately 7. The tested sheets were placed at an angle of $20^\circ \pm 5^\circ$ in the chamber, exposed to the salt fog for a certain period.

3. RESULTS AND DISCUSSION

3.1. Surface morphologies and composition analysis

Fig. 1 showed that the specimen without passivation film had high surface roughness and many holes in dendritic gap. Surface of the sample showed a complete continuous layer of zinc electrodeposition. The figure also showed that after passivation the surface became clear smooth, roughness decreased, but there were structural chap.

Fig. 2 and Table 1 showed that the Chemical Constituents were different between the smooth region A and the chap place B of passivation film. The element contents of Zn and Fe were lower significantly in the place of A than B, however the contents of O, P, S, Cr were higher. The passivation film was uniform dense in the smooth region, it was thinner in the chap place and contained more Zn and Fe.

3.2. Fracture surface morphology and composition analysis

Fig. 3 showed that Zinc coating, passivation film and Fe matrix combined closely, and no defects appeared such as crack. The total thickness of zinc coating and passivation film reaches $12.423 \mu\text{m}$, and dark green passivation film is $1.734 \mu\text{m}$. Passivation film was uniform and dense, galvanized coating presented beautiful equiaxed zinc spangle.

Fig. 4 showed that the distribution intensity of Chromium, oxygen, phosphorus was significantly

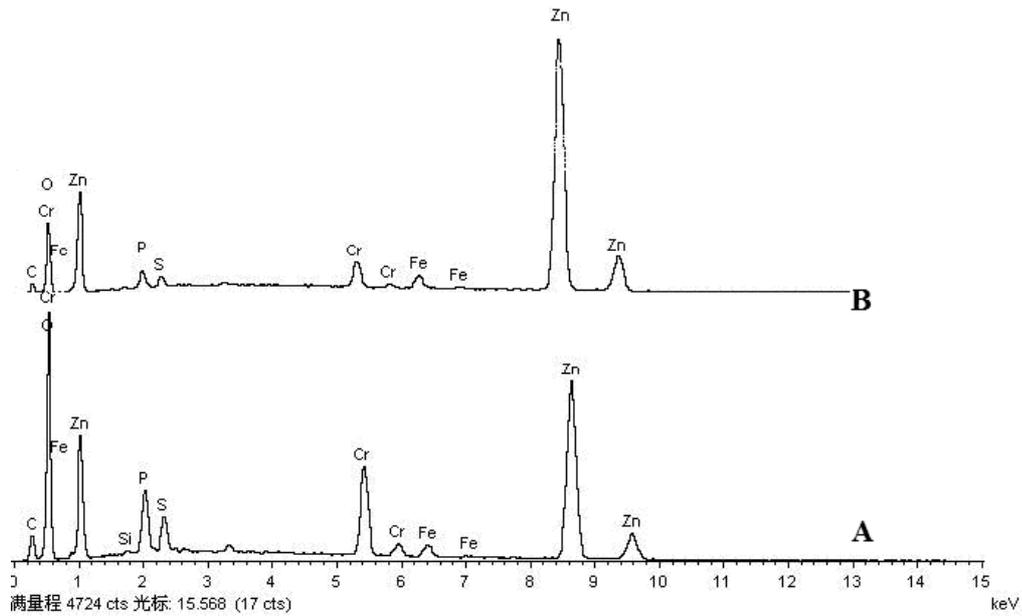


Fig. 2. EDS patterns of different positions on blackishgreen colored passivation film in Fig. 1.

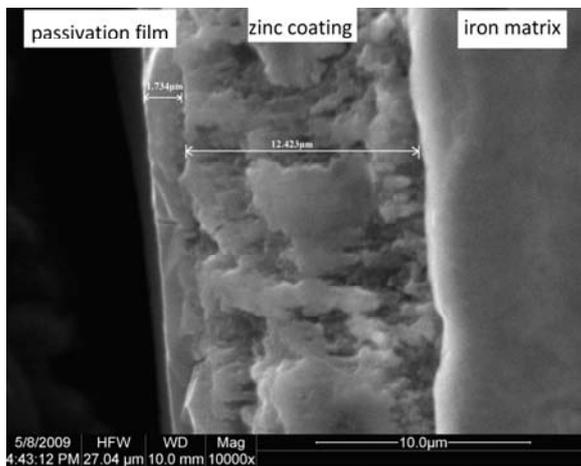


Fig. 3. Fracture surface SEM morphology of specimen with blackishgreen colored passivation film.

higher and S was slightly higher in passivation film than in zinc coating, however the distribution intensity of Zinc, Chlorine was higher in zinc coating than in passivation film. Chlorine occurred in the

galvanized layer, due to use of the electro-galvanized zinc chloride-based environmental protection technology, the main group was divided into the bath KCl, ZnCl, H₃BO₄, and thus Cl-residue presented in the zinc coating. Oxygen, sulfur, and phosphorus in the zinc layer is a result of brightener added in Zinc plating process while remaining in the galvanized layer. Chromium, Oxygen, Phosphorus, and Zinc element was significantly higher in the passivation film than in the galvanized layer that were composed of blackishgreen colored passivation film.

3.3. XRD analysis of passive film

Fig. 5a presents X-ray diffraction patterns of dark green passivation samples. As shown, there were Zn diffraction peaks in the diffraction pattern. We believed that these peaks were produced by electro-galvanized layer coated on the iron matrix. To this purpose, detection of X-ray diffraction was done on the galvanized samples without passivation. Test

Table 1. Element distribution comparison between the smooth region and the chap place of passivation film.

Element		O	P	S	Cr	Zn	Fe
Position A	wt. %	35.73	4.42	2.24	8.35	48.06	1.21
	at. %	66.41	4.25	2.07	4.78	21.86	0.64
Position B	wt. %	14.40	1.67	0.85	2.51	79.02	1.56
	at. %	42.69	2.37	1.17	2.13	53.41	1.23
comparison	Δwt. %	59.70	62.22	62.05	69.94	-64.42	-28.93
	Δat. %	35.71	44.24	43.48	55.44	-144.33	-92.19

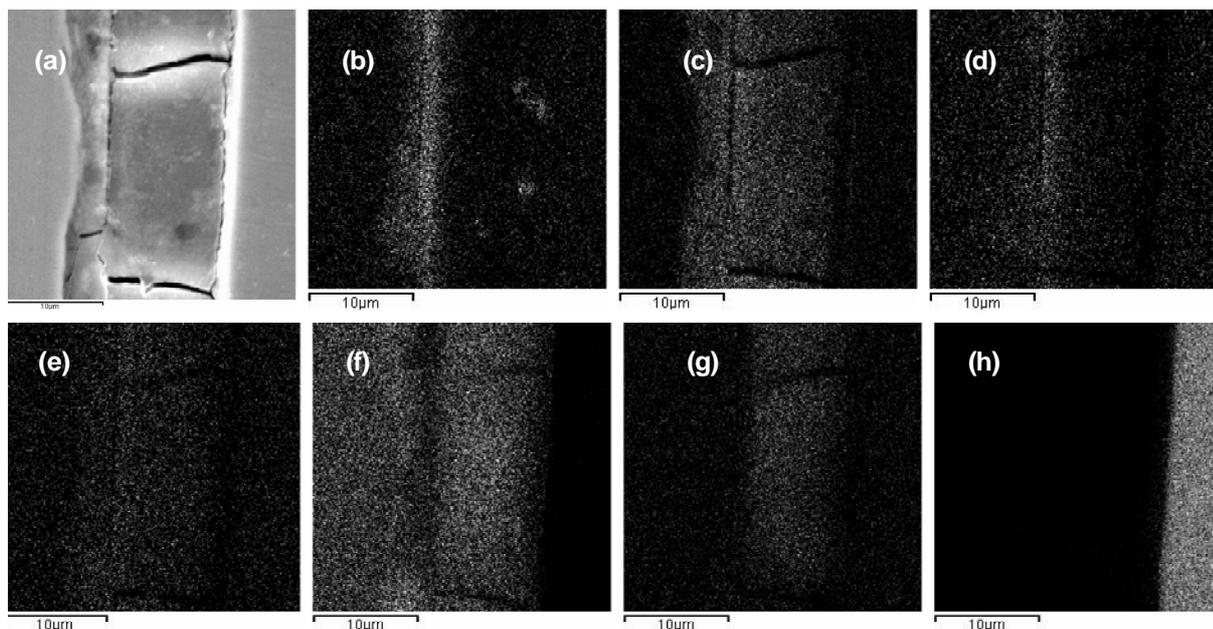


Fig. 4. Fracture surface EDS surface scan analysis of specimen with blackishgreen colored passivation film: (a) Fracture surface SEM morphology of specimen; (b) Chromium; (c) Oxygen; (d) Phosphorus; (e) Sulfur; (f) Zinc; (g) Chlorine; (h) Iron.

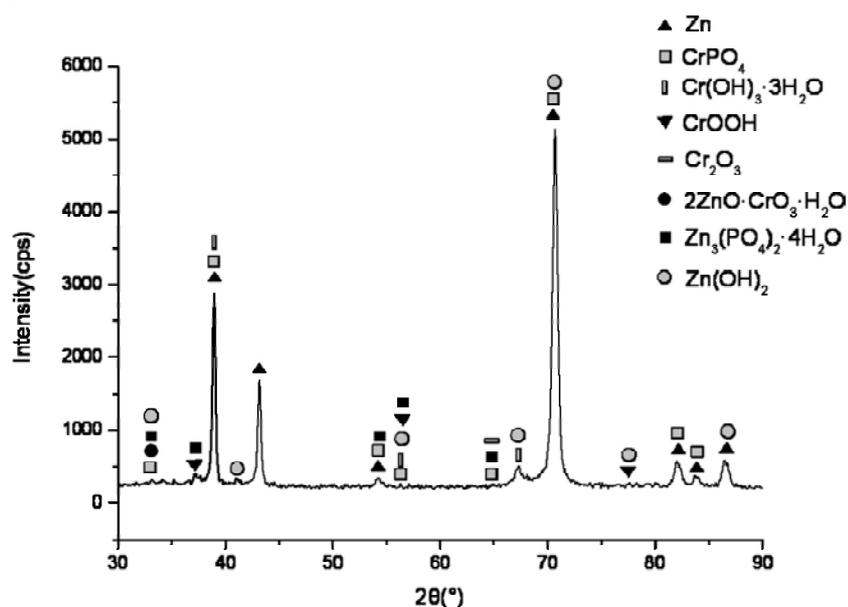


Fig. 5. XRD patterns of the specimens with and without blackishgreen colored passivation film: (a) Specimen with blackishgreen colored passivation film; (b) Specimen without passivation film.

results are shown in Fig. 5b. The six diffraction peaks were all Zn peak in Spectrum 5b, and all the diffraction peaks were relatively sharp, indicating high crystallinity of Zn [3].

Jade5.0 software was used to analyze the data of XRD experiments, The X-ray diffraction pattern showed that there were green and gray blue sticky precipitate CrPO_4 , Cr(OH)_3 , and CrOOH , dark green crystal of chrome green Cr_2O_3 , they did not dissolve in water, which together formed gel compounds col-

loidal film of large network structure [4]. At the same time, there were also excellent anti-corrosion $2\text{ZnO}\cdot\text{CrO}_3\cdot\text{H}_2\text{O}$ and $\text{Zn}_3(\text{PO}_4)_2\cdot 4\text{H}_2\text{O}$ which adsorbed or embedded in the gel film. Other, there were metal Ag that formed as the toner was reduced by contacting with the metal Zn coating, its inclusion in the passivation layer increased the black degree of film, which photographic film as a very fine silver grains scattered on a dark color in the same light-sensitive film. It is like a very fine silver grain in pho-

tographic film scattered on the light-sensitive film displaying in black [5]. All these phases common formed the dark green passivation film with high corrosion resistance.

3.4. Neutral salt spray test of passivation film

The results showed that: The time for corrosion products of specimen without passivation film appearing was 8 h. High surface roughness and many holes in dendritic gap that easily lead to corrosive media enriching in the defect and manifested as localized corrosion preferentially occurred [6]. The time for corrosion products of specimen with blackishgreen colored passivation film appearing was 400 h, although the passive film was thin and there were chap places, But it could effectively suppress the early stages of corrosion of zinc coating and Change the corrosion process [7]. Mao-zhong, et al. [8] studies had shown iron metal enrichment in Zinc coating/passivation film interface could inhibit the corrosion reaction. When the corrosion medium corroded to the coating surface through the passive film, Zn^{2+} would react with water to $Zn(OH)_2$ that in turn decomposed into ZnO and water, in other words, the corrosion medium would oxide Zinc in the Zinc coating. Ferrous metals containing in the coating inhibited the $Zn(OH)_2$ decomposition. When the concentration was high enough, the reaction could be completely inhibited. $Zn(OH)_2$ that uniform covered at the surface of the zinc coating which structure was more compact relative ZnO inhibited the corrosion reaction to some extent. In other wordes, the surface cracked structure would enhance the corrosion resistance of blackishgreen colored passivation film. It was shown that the blackishgreen colored passivation film on the Zinc coating could significantly improve the corrosion resistance of zinc coating. The time for white corrosion products of specimen with blackishgreen colored passivation film appearing was far more than the national standard 96 h and enterprise standard 200 h requirements.

From neutral salt spray test results, dark green passivation film had high corrosion resistance, because of the protective effect from magnesium chromate and its hydrates of trivalent chromium and hexavalent chromium. Trivalent chromium compound acted as a framework in the dark green passivation film by its insoluble in water and high strength. Hexavalent chromium compounds film-forming attached trivalent chromium compounds by its soluble in water and soft. When the passive film had mild injury, hexavalent chromium compounds

in the humid air was soluble in water and generated chromic acid that reacted with the exposed zinc coating. In other words, this was re-passivation to achieve self-repair and maintain the corrosion resistance of the membrane [2].

Divalent zinc ions in passive film came from the zinc coating. Zinc dissolved in the interface layer between metal and passivation solution by the presence of acid and oxidation of chromic anhydride after the zinc coating immersing passivation solution. In this interface layer, pH rapidly increased, and simultaneous hexavalent chromium reduced to trivalent chromium that formed colloidal skeleton of film in alkaline membrane, then the pH could not too high, otherwise the colloidal membrane was dissolved by hydrogen ions. It must be strictly controled that the pH value in the range of 1 to 1.5 to form pH gradient in the film, in order to achieve the balance between membrane dissolution in solution side and membrane formation in Zinc surface side, at the same time, black metal ions also spreaded to the passivation film. This process should be completed within 35~60 s, zinc layer would be Continuous consumption that coule result unnecessary losses if you continued to extend the time. After the samples leaved the passivation solution, the passive film proper stayed 60~120 s in the air that was conducive to the continuation of the surface passivation film forming reactions and membrane thickening.

4. CONCLUSIONS

(1) The Appearance of blackishgreen colored passivation film prepared by passivation technique developed was glossy, homogenous, dense dark green. The time for white corrosion products of specimen with blackishgreen colored passivation film appearing in neutral salt spray test was far more than the national standard 96 h and enterprise standard 200 h requirements.

(2) Sample surface before passivation presents a complete electro-galvanized layer. After passivation the sample surface becomes clear smooth, but there were chaps, the chap place of passivation film was thin and rich in zinc and iron, surface chaps did not affect the corrosion resistance of passive film.

(3) Zinc coating, passivation film and Fe matrix combined closely, and no defects appeared such as crack. Dark green passive film mainly contained chromium, oxygen, phosphorus, zinc, and composed by $CrPO_4$, $Cr(OH)_3$, $CrOOH$, Cr_2O_3 , $Zn(OH)_2$, $2ZnO \cdot CrO_3 \cdot H_2O$, $Zn_3(PO_4)_2 \cdot 4H_2O$, and Ag.

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