Trivalent Chromium Conversion Coating Formed on Hot Dip Zn-55Al-1.6Si Coated Steel

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Abstract. Trivalent Chromium Process (TCP) coating on hot dip Zn-55Al-1.6Si coated steel was investigated by XPS, SEM and EDS. The XPS revealed that aluminium oxides enriched the conversion coating surface. SEM and EDS analyses indicated that composition and microstructure of the conversion coating were not uniform on the dendrite and inter-dendrite regions within the Zn-Al alloy coating, and a small amount of spherical precipitation with the same composition as the conversion coating was detected in the zinc-rich inter-dendrite region. The optimal forming parameters of dilute passivator determined by salt spray test and orthogonal test is: 40°C, 50 vol.% and 3 min. In addition, the salt spray corrosion resistance of the optimal conversion coatings can reach 192 h, and the optimal TCP coating can reduce the cathodic corrosion current density in 0.05 M NaCl solution by an order of magnitude due to the electrochemical polarization measurements.

1. Introduction
Hot dip coated steel (Zn-55Al-1.6Si) is widely used in hardware decoration, automotive industry and other fields [1-2]. Trivalent chromium passivation process (TCP) can form trivalent chromium Cr (III) chemical conversion coating on the surface of zinc, aluminum and other alloys, thus it has significant potential to enhance the corrosion resistance of hot dip coated steel. Moreover, the trivalent chromium passivation technology will be the focused research in this field due to the environmental injunction and the global emphasis on eliminating hexavalent chromium [3-4].

However, due to the special surface condition of Zn-55Al-1.6Si hot dip coating (containing zinc-rich inter-dendritic region and aluminium-rich dendrite region), the formation process of trivalent chromium chemical conversion coating on its surface is different from that of common various aluminum alloys.

In this study, Cr (III) Alodine 5928 passivator was applied to Zn-55Al-1.6Si hot dip coating surface. Moreover, the optimum technological forming parameters was determined by corrosion results of neutral salt spray tests and the composition and structure characteristics of the thin conversion coating were determined by optical high resolution surface analyses.

2. Experimental Methods
Commercialized hot dip Zn-55Al-1.6Si coated steel (hereinafter referred to as Zn55Al) was used as the experimental materials. The hot dip alloy coatings present on both sides, 20-25 μm thick, the specific coating and substrate composition are shown in table 1 respectively. Panels (0.8 mm thick) were mechanically cut into dimensions of 50×50 mm or 15×15 mm for salt spray tests, surface
characterization techniques and electrochemical measurements. They were then cleaned followed by immersion in acetone, ethanol and deionized water. Before the trivalent chromate conversion process, chemical pre-treatment were then employed to the cut panels: etching for 0.5 min in 5 wt.% sodium hydroxide solution at 50°C and desmutting for 10 s in 10 vol.% nitric acid (99.9%) at 25°C.

Table 1. Coating and matrix composition of hot-dip steel panel (wt.%).

| Elements    | C  | Mn  | Si  | P  | S  | Al  | Zn  | Fe  |
|------------|----|-----|-----|----|----|-----|-----|-----|
| Matrix     | /  | /   | 0.34| /  | /  | 52.14| 37.66| 1.62 |
| Hot dip coating | 0.035 | 0.220 | 0.008 | 0.012 | 0.008 | 0.049 | /   | 99.67 |

To form the conversion coating, the degreased and deoxidized specimen (as described above) was immersed in the RTU Bonderite T-5928 coating bath (pH 3.63) at 40°C for deferent time (2 min, 3 min and 6 min), with very gentle periodic beaker agitation, as needed, to dislodge any gas bubbles (H₂) that formed on the metal surface.

A Nava Nano SEM450 microscope associated with an integral EDS detector, operated at an accelerating voltage of 15 kV, were used to investigate surface morphologies and compositions. The chemical states of coating species were determined by X-ray photoelectron spectroscopy (XPS), using an ESCALAB 250Xi system equipped with an Al/K Alpha source. The microfocus monochromator was operated at a spot size of 500 µm, etching depth was about 10 nm, including the dendrite and inter-dendritic regions and the high resolution intensities of the Cr 2p, Zr 3d, O 1s, Al 2p, Zn 2p, etc. photoelectron lines were recorded separately. The background intensity was subtracted from the spectra using the Shirley method. All data were corrected by a linear shift such that the peak maximum of the C 1s binding energy of adventitious carbon corresponded to 284.6 eV.

For the electrochemical measurements, a three-electrode cell was used, with a Solartron 1287 potentiostat system. The cell contained an Ag/AgCl/Cl⁻ (saturated KCl) electrode, a platinum sheet counter electrode and a working electrode with an exposed area of 1 cm². Measurements were carried out in naturally aerated or nitrogen deoxidizing 0.05 M NaCl solution at room temperature. The cathodic polarization curves was obtained by scanning the potential from OCP to 0.15 V vs. the OCP, with a scanning rate of 1 mV/s. CView software (version 3.1) was used to fit the experimental data.

The salt fog test was conducted according to ASTM B117 (5 wt.% NaCl). At the end of the test period, the specimens were removed, rinsed thoroughly with ultrapure water, and dried under a stream of N₂ gas. After photos were taken by Canon digital camera, any corrosion product was removed by ultrasonication (room temperature) in ammonium acetate acid.

3. Results and Discussion

3.1. Optimization of Processing Parameters and Neutral Salt Spray Test

To verify the applicability of the two kinds of passivating agents to the Zn55Al, orthogonal tests with three factors and four levels were designed to determine reasonable technological parameters, and the operating conditions are listed in table 2. The appearance corrosion rating of each group of samples after the 192-h NSS test was assessed based on ISO 10289, and was used as quantitative criteria in the orthogonal test. The optimal experimental parameters are shown also in table 2. The order of the influence of parameters obtained from the orthogonal test result shows that the concentration is the primary influencing factor, and the next two are the temperature and time.

Figure 1 is the surface photos of the panels treated with 9 sets of test parameters under 0 h, 96 h and 192 h salt spray corrosion. After corrosion in a salt fog environment for 96 h, the corroded area exhibited a coating deterioration type of “J” (Crow’s feet or star-shaped defects type). The black corrosion zone spreads from the edge of the sample to the center, marked by the red scissors in the figure 1(b). This may be due to the imperfection of the epoxy seal at the specimen edge or the poor TCC formation in the edge regions [5]. In addition, when the corrosion proceeded to 192 h, not only new corrosion areas appeared, but also the original corrosion areas increased in varying degrees, as shown by the red elliptical markers in figure 1(c).
### Table 2. Preset experimental parameters of orthogonal design and optimal experimental parameters.

| Passivator     | pH     | Concentration (vol. %) | Bath temperature (°C) | Immersion time (min) |
|----------------|--------|------------------------|------------------------|----------------------|
| Preset parameters | 3.4/3.6/3.8 | 30/40/50 | 30/40/50 | 2/3/6 |
| Optimal parameters | 3.6 | 50 | 40 | 3 |

![Figure 1](image1.png)

**Figure 1.** Samples after (a) 0 h; (b) 96 h and (c) 192 h salt spray tests treated with combination of different Alodine 5928 passivation parameters in orthogonal test.

### 3.2. Surface Morphology and Chemical Composition of the Pretreated and Conversion Coated Specimens

Overview XPS spectra for optimal Alodine 5928 treated Zn55Al sample surface is shown here in figure 2. The atomic percentage of the main elements is shown in table 3.

The XPS analysis shows the content of major elements on the surface of the passivated specimen. The intensity ratio of Zr 3d to Cr 2p was fixed at 1.76:1. This proportion is consistent with previous studies [6]. In addition, nearly 8.6 at.% of F element was detected. The concentration of $F^-$ in passivation water sample is about $9.29 \times 10^3$ ppm by means of Metrohm 883 IC ion chromatograph, which indicates that the passivator has a strong oxidation property [7]. Additionally, the passivation solution also contains about 118.8 ppm $Cl^-$ ions and 72.2 ppm $NO_3^-$ ions, which probably originates from $Cr_2(SO_4)_3$ or $CrCl_3$ in the Alodine 5928 formulation.

![Figure 2](image2.png)

**Figure 2.** Overview XPS spectra for Alodine 5928 treated Zn55Al surface (optimal sample).
Table 3. Atomic (%) table of main elements for optimal Alodine 5928 treated Zn55Al by XPS.

| Element | Zr 3d | F 1s | Cr 2p | O 1s | Zn 2p | Al 2p | C 1s |
|---------|-------|------|-------|------|-------|-------|------|
| Atomic (%) | 6.73  | 8.6  | 3.82  | 26.96| 2.54  | 15.64 | 35.73|

The examination of the chemical states of coating species was carried out using high-resolution spectra for the O 1s, Al 2p, Zn 2p, Zr 3d and Cr 2p regions. Due to the limitation of space, it is not shown here. The fitting results showed that about 45.11% of the substances of the chemical conversion coating were oxides at a depth of 10 nm, most in the form of alumina. In addition, a small amount of AlF₃ and ZrF₄ were also detected during the fitting analyze in high-resolution spectra of Al 2p and Zr 3d. A small amount of Cr (VI) ~1% appeared in the formed TCP coating after it was placed in air for a period of time, which may be related to the oxidation of the conversion film with aging; however, the appearance of hexavalent chromium can play a role of "self-healing" for the thin film to a certain extent. Its mechanism and the shelf in the conversion film need further exploration [8].

Zn55Al can be inferred to be passivated by the film formed from the trivalent chromium solution in the following formation process: (i) the zinc and aluminium in the hot-dip coating are oxidized to Zn²⁺ and Al³⁺ ions in the acidic trivalent chromium passivation solution; (ii) with the progress of oxidation and oxygen reduction reaction, a large amount of hydrogen ions are consumed in the reaction between the panel and the solution interface, and the consumed hydrogen ions cannot be replaced, resulting in a rapid rise in the pH and the formation of a thin alkaline layer; (iii) when the gel film formed from the trivalent chromium solution is dried after washing with water, some of the hydroxide is oxidized to oxide, forming a conversion coating composed mainly of oxide blends with extra hydroxide.

Figure 3 reveals a cross-section SEM micromorphology of the optimal Alodine 5928 treated Zn55Al sample and EDS elemental maps of aluminium, oxygen, zirconium, chromium and fluorine. It indicates the preferential precipitation of zinc in zinc-rich inter-dendritic regions due to the cathodic behavior of de-alloying process, leading to the heterogeneous film formation of the conversion film [9]. It is inferred that the preferential dissolution of zinc in the inter-dendritic zinc-rich phase provides a powerful impetus for the film formation process. This results in a slightly larger thickness of the chemical conversion film in the interdendritic region, and obvious spherical precipitation is found, indicating that the redox reaction here is more intense [10-11].

Figure 3. Composition and structure of Zn55Al surface with optimal Alodine 5928 treatment: (a) SEM micromorphology and (b) EDS elemental maps.
Figure 4. Slow-scan cathodic polarization curves for uncoated Zn55Al and Cr (III) coated Zn55Al in aerated and de-aerated 0.05 M NaCl.

Table 4. Fitting results of cathodic polarization curves recorded in figure 4.

| Samples                              | $E_{corr}$ (V) | $i_{corr}$ (A/cm²) |
|--------------------------------------|----------------|--------------------|
| Uncoated Zn55Al in aerated 0.05 M NaCl | -0.8936        | 2.13E-07           |
| Uncoated Zn55Al in de-aerated 0.05 M NaCl | -0.9305        | 5.21E-08           |
| Cr(III)-coated Zn55Al in aerated 0.05 M NaCl | -1.0598        | 4.81E-08           |

3.3. Basic Electrochemical Properties of the TCP Coating

In figure 4, the cathodic corrosion current density of uncoated Zn55Al at corrosion potential is much smaller in the de-aerated 0.05 M solution, compared with the current density in the aerated solution. The presence of oxygen accelerates the corrosion process by depolarizing the cathodic areas [8]. Since the corrosion of Zn55Al surfaces takes place under cathodic reaction control, it follows that a reduction in the corrosion rate can be brought about by inhibiting the cathodic reaction. The corrosion of Zn55Al bare surface can be retarded by hindering the transport of oxygen to the interface [12]. As shown in figure 4 and table 4, although the TCP coating is very thin, cathodic current at potentials close to $E_{corr}$ measured on Cr(III) treated Zn55Al sample in the aerated 0.05 M NaCl solution is significantly smaller than that on the bare sample, to an extend of an order of magnitude (with 2.13E-07 V and 4.81E-08 V separately). Hence, it is clear that Cr (III) coatings formed an effective barrier layer which hindered the transport of oxygen to the Zn55Al substrate.

4 Conclusions

In this paper, the optimal experimental parameters for the formation of chemical conversion coating on Zn-55Al-1.6Si coated surface using Cr (III) Alodine 5928 passivator were obtained as follows: 3 min to formation time, 40°C to passivation temperature and 50 vol. % to dilute concentration. The thin layer of TCP is aluminium-rich, with the presence of oxide and fluoride species, and the less than 1% of the Cr (VI) exists on the surface of the conversion coating. In addition, the neutral salt spray corrosion resistance of this thin film can reach nearly 192 h and TCP coating can inhibit Zn55Al corrosion in dilute NaCl solutions by hindering the transport of oxygen to the substrate metal. The electrochemical polarization results indicate that the cathodic corrosion current of Alodine 5928-treated Zn55Al sample is an order of magnitude smaller than that of untreated sample.

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