Corrosion Resistance of Hot-dip Zn55Al Coated Steel Sheet Treated by Cr(III) Conversion Coating Against Chloride-Containing Media

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Abstract. Under the influence of chloride-containing environment such like shallow sub-marine or littoral area, hot-dip Zn55Al coated steel sheet is easily corrode. Based on an applicable combination of parameters, a Cr(III)-based conversion coating(TCC) was formed on Zn55Al coating successfully based on Coldip 120 commercial passivator. The corrosion behaviour of the Cr(III) treated hot-dipped steel samples subjected to the Cr(III)-based passivation treatment was studied using electrochemical impedance spectroscopy (EIS) in a 3.5% NaCl solution, and the failure mechanism of the conversion coating-hot-dip coating system was investigated by analysing the time dependence of the electrochemical parameters of impedance. In addition, the role of corrosion products formed on Zn55Al during the different immersion time in the NaCl solution was also revealed by scanning electron morphology (SEM) and energy dispersive spectrometer (EDS).

1. Introduction
Hot dip Zn-Al alloy coating has been used commercially for about 50 years. Zn–Al alloy coatings for steel were developed with an anticorrosive performance superior to that of each of the metals used individually [1, 2]. The high corrosion resistance of aluminized coating combined with the excellent cathodic protection afforded by galvanized coating to the substrate both contribute to their superior performance. Zn–55Al–1.6Si coating, better known as Galvalume, introduced during the 1970s which was used for marine environments in most cases [3, 4].

The trivalent chromate conversion coating (CCC) technology was commercially introduced in the late 1980s as an early attempt to replace carcinogenic hexavalent chrome from as many metal finishing processes as possible [5]. Studies performed by Wen and Bellezze revealed that Cr(III) coatings formed on electrogalvanized steels through sealing treatments have a corrosion resistance comparable to that imparted by the Cr(VI) passivation treatment according to electrochemical methods and salt spray tests [6, 7]. However, the formation of cracks during the baking and dehydration process deteriorates the corrosion resistance of the conversion coating [8]. The results obtained from EIS measurements can provide insight into the electrochemical characteristics of the tested conversion coatings, and impedance measurements at very low frequencies have allowed the detection of interfacial processes not accessible by polarization curves [9]. And qualitative comparison of the coating corrosion resistances can be accomplished from simple visual analysis of the time dependence of the |Z| and phase angle values.

Many investigations and valuable results related to the corrosion behaviour of conversion coatings on galvanized coatings have been reported, but extensive fundamental research is still needed to elucidate the suitability of hot-dip coating sheet to Cr(III) based passivators and the mechanism of the
corrosion performance against chloride-containing media. A low concentration chromate passivation treatment has been successfully processed on Zn25Al by previous research, but it was Cr(VI) based [10]. In the present paper, natural exposure tests combined with electrochemical measurements have been applied to evaluate the performance of the Zn–55Al–Si coated steel sheet in 3.5% NaCl solution.

2. Experimental Methods

2.1. Preparation of Test Samples
Zn-55Al-1.6Si (Zn55Al) coated steel sheets (50×50×2 mm) were chemical converted using a commercial Cr(III) based passivator: Coldip TRI-V 120 (hereinafter referred to as Coldip 120). The operating conditions were immersion time 4 min, treatment temperature 40°C, and dilute concentration 15 vol.%. The passivation process of the test specimen was carried out in a plastic beaker to avoid reaction between the fluorine ions in the passivating agent and the silica in the glass container. A heater with magnetic stirrer was used to provide heat for the passivation process. After treatment, the passivated samples were again rinsed with deionized water and then dried in a desiccator at room temperature for 24 h. Zn55Al sheets were first cleaned by acetone using ultrasonic cleaner for 20 minutes at least to remove the fingerprint-resistant coating on the surface before the Cr(III) treatment, and the surface was cleaned by every 5 minutes.

2.2. Electrochemical Impedance Spectroscopy Measurements
Open-circuit potential (OCP) and EIS measurements were carried out in a glass electrolytic cell specifically designed for these measurements. The test specimen was sealed in the lower part of the electrolytic bath. The exposed area of the coated surface was ~12.6 cm². The test piece was sealed in the lower part of the electrolytic bath. The reference electrode was an Ag/AgCl/Cl⁻ (saturated potassium chloride) electrode, and the counter reference was a carbon electrode. EIS measurements, as a function of the exposure time in quiescent and open to air 3.5% NaCl solution (pH=6) at room temperature, were conducted using a Solartron 1255 frequency response analyser coupled with a Solartron 1287 potentiostat (both controlled by the Zplot program). The frequency range of the impedance response was 10 kHz to 0.01 Hz with a small potential perturbation (5 mV a.c. amplitude around the OCP). All the impedance data of the Zn55Al samples with Cr-(III) conversion coatings in 3.5% sodium chloride were modelled and interpreted using the ZsimpleWin software fitting procedure. Before each electrochemical impedance spectroscopy test, the open-circuit potential must be re-detected and wait for its stability before it can start. The most representative experimental results are presented in this paper.

2.3. Semi-Quantitative Chemical Analyses and Morphology
The morphology of the coating surface was examined by field-emission high-resolution scanning electron microscopy (SEM, Nava Nano SEM450), while the associated compositions of the coating were measured by energy-dispersive X-ray (EDS) spectroscopy with a 15 keV energy.

3. Results and Discussion

3.1. Impedance Measurements
EIS measurements on Cr(III) treated Zn55Al samples as a function of the immersion time in a 3.5% NaCl solution were carried out to monitor the evolution of the electrochemical behaviours. The EIS data at 1 h, 6h, 12h, 24h, and 48h of immersion were obtained.

The representative Nyquist plots obtained within 48 hours of corrosion are shown in figure 1. At first glance, a comparative evaluation of the coating corrosion resistance was carried out by observing the values of both the |Z| at low frequencies and the maximum angle phase. At the beginning of immersion, the permeating and corrosion-inducing chemicals (water, oxygen and ionic species) reach the electrochemically active areas of the hot-dip substrate through the conversion coating defects. The Nyquist plots of 1h (figure 1) shows a well-defined second arc at low frequency, which was observed as well by the corresponding phase angle plot (figure 2).
described by the equivalent circuit proposed in figure 3. In the model shown in figure 3, Rs models the resistance of the electrolyte. The first time constant that appears at higher frequencies represents the micropore resistance of conversion coating (R₁) and the conversion coating dielectric capacitance (CPE₁). The parameters R₂ and CPE₂ account for the charge transfer resistance and the electrochemical double-layer capacitance of the corrosion process.

Figure 1. Nyquist plots and the equivalent electric circuits obtained on the Coldip 120-treated Zn55Al sample in a 3.5% NaCl solution for short immersion time.

After 6h of immersion, the corrosion reactions take place on parts of the surface exposed to the NaCl solution through pores or defects of the coating. With the diffusion control reaction or sorption processes taking place on the reactive surface, the second loop (i.e. the low frequency loop) of both samples changed significantly its shape, displaying a distortion and suggesting an electrochemically active interface [11]. From figure 2, the improved impedance |Z| value could be explained by assuming that the accumulation of the corrosion products within the pores and/or other coating defects. After 12 hours of corrosion, the impedance |Z| value reached its maximum value with an apparent shift towards lower frequency of the position of maximum theta value compared to 1 h. The initially loose corrosion products tended to become more compact at this period and the shit of the position of the maximum theta value might be related to the change of corrosion resistance property of the porous conversion coating.

Figure 2. Bode plots showing the time dependence of impedance for different immersion periods: (a) Change of phase angle with frequency and (b) Change of |Z| with frequency.

Figure 3. Equivalent circuits used to model the Cr(III) treated Zn55Al in a naturally aerated 3.5% NaCl solution for 48h.
Figure 1 and figure 2 also reveal the impedance of the later stage of corrosion (24-48 h). The corresponding maximum theta value and the |Z| value at low frequencies both decreased at this period, which indicates a stable corrosion product layer is formed on the Zn55Al surface and the partial loss of the conversion coating dielectric capacity. At this time, the corrosion products are thicker, but the transport channel of the corrosion-inducing chemicals between metal matrix and electrolyte is broader than that of the initial stage of corrosion. Therefore, the chemical conversion film has basically lost its protective effect, and the whole corrosion product layer/conversion coating/Zn55Al system is in a stable state.

3.2. SEM-EDS Analyses of the Cr(III) Treated Zn55Al Surfaces

To establish whether the increased impedance is due to the formation of corrosion products on the Cr(III) treated Zn55Al sheets, scanning electron photographs were taken (figure 4a-d) for different immersion time.

Figure 4b after 24h, 5c after 48 h and 5d after 72 h immersion in NaCl solution showed a rough and perished surface while the surface with 12 h corrosion (figure 4a) was less corroded and smooth especially in the dendritic regions. In figure 4b, the lamellar material with strong adhesion between dendrites has not been removed. Elemental analysis of EDS energy spectrum focused on showed that it may be needle-like Si-rich phase in hot-dip coating. In figure 4d, after 72 hours of corrosion, some corrosion products still adhere to the interdendritic zone on the surface of Zn55Al after cleaning. The EDS analysis revealed that the products are mainly composed of zinc or aluminium oxides. The ratio of zinc to aluminium is close to 0.8, and the other elements are mainly oxygen. Previous research reported that the corrosion product of the coating in seawater were probably produced by the co-precipitation caused by adsorption and they are typical nanometer microcrystals, containing Zn₄CO₃(OH)₆·H₂O, Zn₅(OH)₈Cl and Zn₆Al₂CO₃(OH)₁₆·4H₂O [4].

![Figure 4](image_url)

**Figure 4.** SEM micrographs of Cr(III) treated Zn55Al surface with (a) 12 h; (b) 24 h; (c) 48 h and (d) 72 h immersion in a naturally aerated 3.5% NaCl solution at room temperature (The corrosion products on the surface of the corroded samples have been removed).
Figure 5. SEM morphology and EDS spectra of Cr(III) treated Zn55Al alloy surface after 12 h immersion in a natural aerated 3.5% NaCl solution at room temperature without corrosion products cleaning.

EDS spectra were used to determine the elements present on the metal surface before cleaning of corrosion products. Without the cleaning of corrosion products on Zn55Al after immersion in NaCl solution, the corrosion products is obvious. From the SEM morphology of sample observed after immersion for 12 h in figure 5a, the surface of Cr(III) treated Zn55Al tend to be covered by a layer of corrosion product especially at the regions of interdendritic regions, which is generated by the reaction between electrolyte and Cr(III) treated Zn55Al surface. As reported before, the conversion coatings formed at interdendritic regions showed a porous character as compared to dendritic regions [12]. Corrosion products are first generated here, and to some extent will block the pore between dendrites and prevent further corrosion development. The EDS energy spectra corresponding to the label position in figure 5a is shown in figure 5b. According to previous reports, it is assumed that the corrosion products mainly contains di-hydroxides, bicarbonates and chlorides of zinc and aluminium.

4. Conclusions
With the prolongation of corrosion time, the surface impedance modulus (|Z|) value of Zn55Al after trivalent chromium treatment increased first and then decreased. The increased corrosion resistance is induced about 6 to 12 h after the immersion. The accumulation of the corrosion products within the pores and/or other coating defects, which improved the barrier protection of the coating temporarily. And the corrosion products mainly contains di-hydroxides, bicarbonates and chlorides of zinc and aluminium.

When the immersion proceeded, the corrosion products on the surface of the conversion film acted as sealants and eventually provided additional protection to the surface of Zn55Al. Although chloride ion has strong penetration, which makes corrosion resistance decrease, the impedance value with longer immersion times at low frequency tends to a relatively stable value, higher than that of the value measured at first.

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