

Short Communication

Comparative EIS Study on Atmospheric Corrosion Behavior of Zinc-Aluminum Coated Steels under Cyclic Wet-Dry Conditions

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Due to the excellent anticorrosion performance, galvanized steels are widely used in a variety of structural applications for corrosion protection of steel structure exposed to atmospheric environment, especially marine atmosphere. In this work, the corrosion behavior of two representative zinc-aluminum hot-dip coated steels, Galvalume(GL) and Galfan(GF), under cyclic wet-dry conditions, was investigated by weight loss method and electrochemical impedance spectroscopy(EIS) measurement. The wet-dry cycle tests were carried out by exposure to alternate conditions of 1h immersion in seawater and drying for 3h and 11h at 298K and 60% relative humidity (RH). During the wet-dry cycles, the polarization resistance was continuously monitored and its reciprocal was considered as an index of corrosion rate. Results show that the anticorrosion performance of GL coating was better than that of GF coating in all tests. The effects of the formation of stable simonkolleite layer and other influence parameters, such as elemental composition of coating materials, on the corrosion of two coated steels were discussed.

Keywords: Hot-dip Coated Steel; Atmospheric Corrosion; Electrochemical Impedance Spectroscopy (EIS); Wet-dry Condition; Corrosion Monitoring

1. INTRODUCTION

Due to the excellent anticorrosion performance, galvanized steels are widely used in a variety of structural applications such as buildings, electrodomestic and automotive industries for corrosion protection of steel structures exposed to atmospheric environment, especially marine atmosphere[1]. During these years, hot-dip coatings, such as Galfan (GF) and Galvalume (GL), are commonly used in

these fields with high demands for more corrosion-resistant materials.

Atmospheric corrosion is the most prevalent type of material corrosion by the interaction of physical, chemical and material factors. According to incomplete statistics, the economic loss due to atmospheric corrosion amounts to almost half of the total corrosion. In the real atmospheric environments, corrosion proceeds under a thin electrolyte layer during wet-dry cycles, and the corrosion process is very different from that in the bulk solutions[2-6].

Due to the high ohmic drop between the reference electrode and working electrode and uneven current distribution over the working electrode, it is technically difficult to conduct electrochemical measurements under the thin electrolyte layer[7]. For a long time, the environment exposure test is the most common means used to study the atmospheric corrosion, which provides average corrosion rate but needs relative long period. These problems have been solved to a certain extent as electrochemical impedance spectroscopy(EIS) is proved to be quite useful technique for the monitoring of atmospheric corrosion[8-11]. In contrast with long-term environmental exposure test, EIS technique provides ample interfacial information in a much shorter time.

Since corrosion behavior of electroplated zinc coated or galvanized steel in chloride solution has been widely discussed[8-14], some results seemed to be controversial. And little report was documented about galvanized steel exposed to alternate condition involving seawater. The aim of this study is to verify the feasibility of EIS technique for the monitoring of atmospheric corrosion in comparison with the common environment exposure test, and corrosion behavior of two representative hot-dip coated zinc-aluminum coatings, Galvalume(GL) and Galfan(GF) are to be evaluated and compared under a wet-dry cyclic conditions involving seawater to simulate marine atmospheric environment. Additionally, the mechanism of the performance will be systemically analyzed in view of influence parameters.

2. EXPERIMENTAL SECTION

2.1. Weight loss experiment

The specimens used in weight loss experiment were 5%Al-Zn (GF) and 55%Al-Zn (GL) coated low carbon sheet steels, with a dimension of 50mm×50mm×2 mm. According to the commercial data, the thickness of GF and GL coating layer was approximately 15~20μm. The specimens were exposed to an alternate condition of 1h immersion in seawater and 3h drying at 298 K and 60% RH, and taken out group by group after 16cycles, 32cycles and 64cycles, with three parallel specimens in each group. The corrosion products covered on the specimen were removed by mechanical method, and the weight of specimen was weighed by digital balance before and after corrosion, respectively. The weight loss was calculated by the weight before corrosion minus the weight after corrosion and average corrosion rate was subsequently achieved.

2.2. Preparation of electrode

A two-electrode cell configuration with the exposed area of 2 cm² each, as shown in Fig. 1, was

used as a probe for the corrosion monitoring. Above-mentioned commercial hot-dip galvanized steel sheet was used as the probe electrode. A pair of identical electrodes cut from the galvanized steel sheet was mounted in an ambient temperature solidifying epoxy resin with the separation gap of 0.1 mm. In order to avoid crevice corrosion on the exposed area and on the edges separating the two metal sheets, they were covered with a thin layer of epoxy resin. To ensure the constancy of electrolyte layer thickness at the onset of each dry cycle, a peripheral bank of 0.5 mm thick was fixed on the electrode surface. During test the cell was exposed to an alternate condition of 1h immersion in seawater and 3h, 11h drying at 298 K and 60% RH.

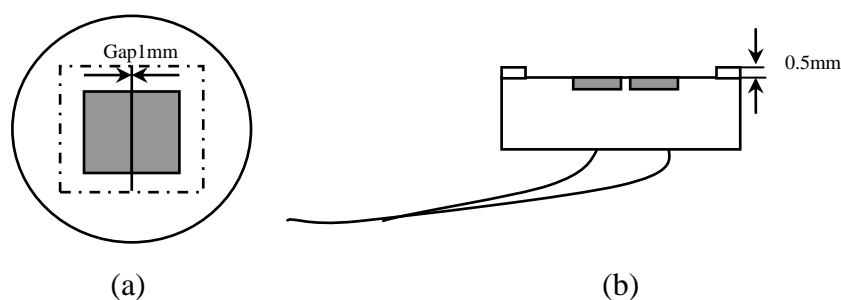


Figure 1. Schematic diagram of a three electrode cell: (a) top view, (b) transverse cross-sectional view

2.3. Electrochemical impedance spectroscopy (EIS) measurement

Continuous monitoring of corrosion of GF and GL coating was performed using a Riken Denshi CT-7 type AC corrosion monitor. Special software was used for data acquisition and this system operated at two frequencies, high frequency, 10 kHz (Z_H) and low frequency, 10mHz (Z_L). The impedances were simultaneously measured at these frequencies, then the polarization resistance, R_p , was given by subtracting the high frequency impedance from the low frequency one as follows[14]:

$$R_p = Z_L - Z_H \quad (1)$$

This is based on the assumption that the high frequency impedance gives a solution resistance and the low frequency provides a sum of solution resistance and polarization resistance.

3. RESULTS AND DISCUSSION

The average corrosion rate calculated from weight loss data of GF and GL coated steel under the alternate conditions after 16cycles, 32cycles and 64cycles was shown in table 1. According to the weight loss experiment, the average corrosion rate decreased with the increase of experimental cycles, and the average corrosion rate of GL coated steel was much lower(almost half) than that of GF, comparatively.

Table 1. Average corrosion rate of GF and GL coated steel exposed to wet-dry conditions

Times of wet-dry cycles		16	32	64
average corrosion rate [$\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$]	GF	92.7	88.7	75.0
	GL	47.7	43.0	37.1

The results of the R_p^{-1} of GF and GL coated steel in the 64 wet-dry cycles, i.e. 256h, monitored by AC impedance technique were shown in Fig. 2 and Fig. 3, respectively. The average value of R_p^{-1} of 16cycles, 32cycles and 64 cycles was shown in table 2.

According to Stern-Geary equation[13,14], i_{corr} can be calculated from R_p value:

$$i_{\text{corr}}=k/R_p \quad (2)$$

where the value of k is a proportional constant. If the equation is adoptable, there should be a linear relationship between i_{corr} and R_p , as well as between the corrosion rate and R_p^{-1} . In order to verify the feasibility of Stern-Geary equation used for the galvanized steel corrosion study, the correlation between the corrosion rate resulted from weight loss experiment and R_p^{-1} was studied as shown in Fig. 4. By regression statistics calculation, the R square of GF and GL coating was 0.942 and 0.996, respectively, which proved the equation was suitable for the system we studied and the value of R_p^{-1} could be considered as an index of the corrosion rate of zinc-aluminum coating.

It was observed in Fig. 2, 3 that the R_p^{-1} of GL coated steel was considerably smaller compared with that of GF coating, indicating that the corrosion rate of GL coated steel was smaller than that of GF coating, which was in good accordance with the result of weight loss experiment. For both GF and GL coated steels, during the entire set of cycles, the R_p^{-1} as the index of corrosion rate continuously decreased with wet-dry cycles. Within each cycle as shown in Fig. 2(b), 3(b), the corrosion rate as well as R_p^{-1} decreased after the specimens were immersed in the solution, and increased with time during the drying process.

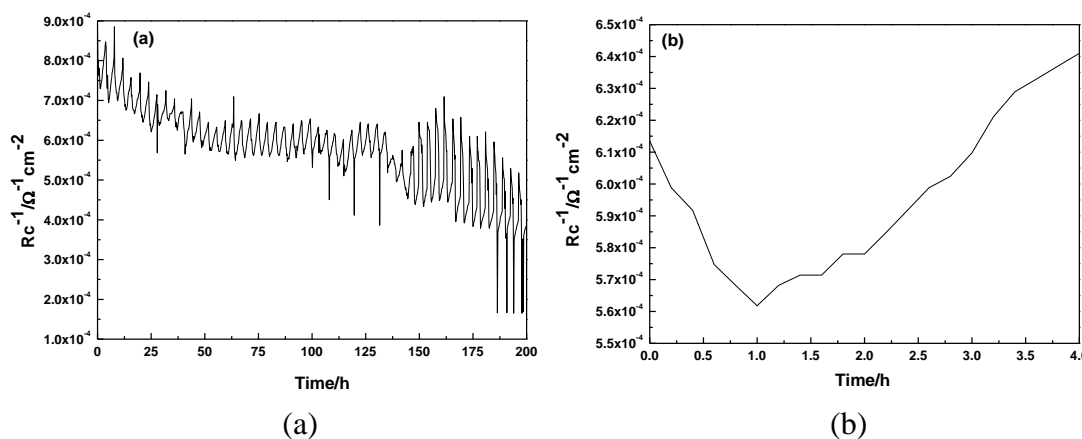


Figure 2. Corrosion monitoring results of GF coated steel under alternate condition of 1h-immersion in seawater and 3h-drying: (a) whole cycles; (b) one cycle

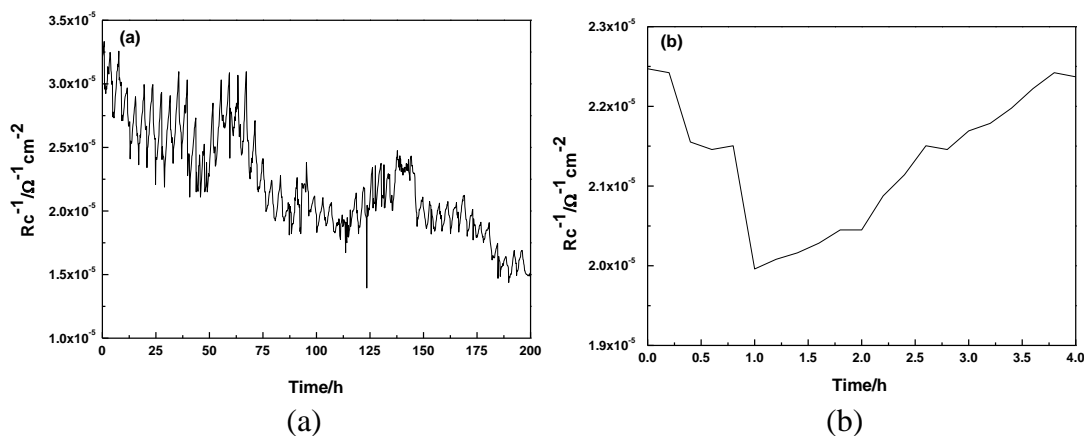


Figure 3. Corrosion monitoring results of GL coated steel under alternate condition of 1h-immersion in seawater and 3h-drying: (a) whole cycles; (b) one cycle

Table 2. The average R_p^{-1} of GF and GL coated steel under alternate conditions

Times of wet-dry cycles		16	32	64
$R_p^{-1} [\times 10^{-5}(\Omega^{-1}cm^{-2})]$	GF	68.8	64.3	58.7
	GL	2.69	2.52	2.25

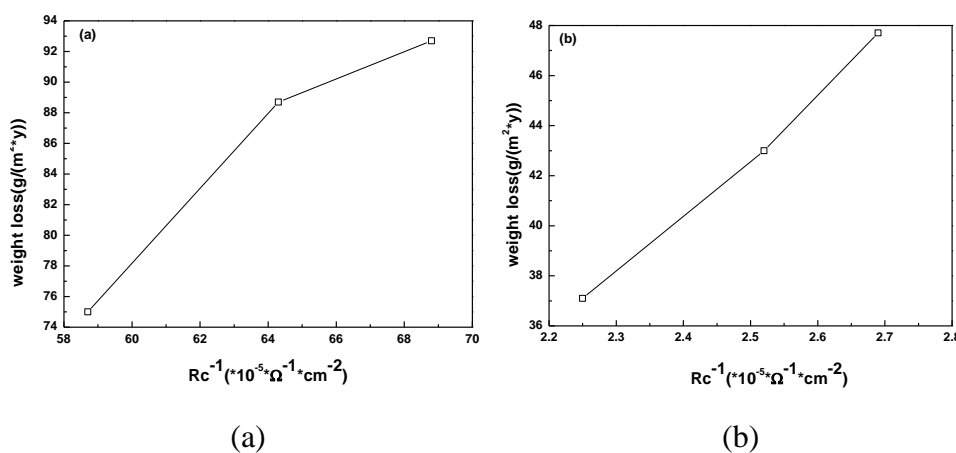


Figure 4. The correlation between R_p^{-1} and average corrosion rate of coated steel (a) GF, (b) GL

The corrosion behaviors of GF and GL coated steels exposed to an alternate condition of 1h immersion in seawater and 11h drying at 298 K and 60% RH were further studied, as shown in Fig. 5, 6. According to the experimental results and above-mentioned method, the corrosion rate of GF coating was also higher than that of GL as the drying period increasing, but the corrosion rate of GF and GL coating were both lower than that above-mentioned condition. According to investigation of Yadav[14], considering the parameter of time of wetness(TOW), shorter drying period in each cycle led to higher amount of corrosion of the coating because the surface was under wet conditions for longer periods.

As shown in Fig. 5 (b), the corrosion behaviors of GF and GL coated steels were completely different. For the GF coating, the corrosion rate was small when the electrodes were immersed in seawater, and sharply increased to a comparatively stable high value when drying. For the GL coating, in the reverse manner, the corrosion rate was obviously higher when immersed in seawater than that dried in atmosphere with a sharp alternation on the boundary.

In the present study the tested anticorrosion performance of GL coating was better than that of GF coating in all the cases. Katayama[15] had studied exposure of galvanized steel in chloride solution with different Al contents, which showed that the addition of Al more than 5 mass% was effective in increasing the corrosion resistance, and attributed it to the formation of aluminum oxide on the specimen surface. It was also proved by the study of Sere[16] and Yadav[17], involving comparative corrosion behaviour of galvanized and zinc coated steels. Also different composition of the corrosion products resulted in different corrosion behavior. For the corrosion process of GL coating with considerable aluminum content, aluminum hydroxide resulted from interaction of aluminate with carbon dioxide in the air decreased the corrosion rate during drying period while it was not adoptable for GF coating.

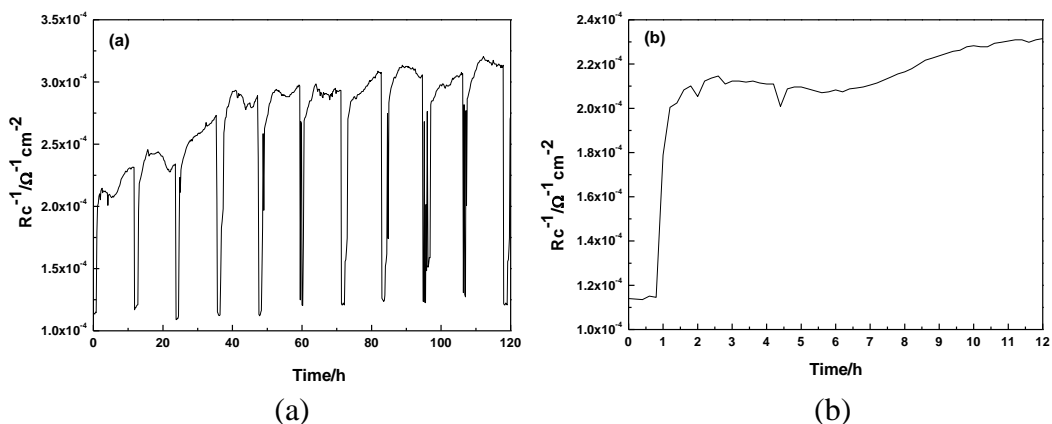


Figure 5. Corrosion monitoring results of GF coated steel under alternate condition of 1 h-immersion in sea water and 11 h-drying: (a) whole cycles; (b) one cycle

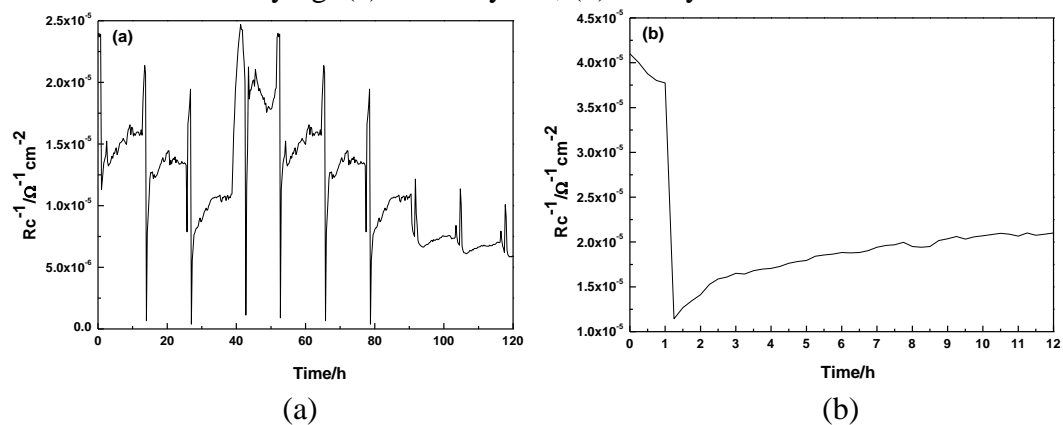


Figure 6. Corrosion monitoring results of GL coated steel under alternate condition of 1 h-immersion in sea water and 11 h-drying: (a) whole cycles; (b) one cycle

Several studies have been focused on the corrosion behavior of galvanized steels under various conditions using AC impedance technique[13-17]. Most of the studies have shown a typical variation of corrosion rate with time, that is, the corrosion of the coating increasingly accelerated for the first several wet-dry cycles, followed by a gradual decrease and finally became constant. Such behavior has been explained by taking account of the role of drying periods available in each cycle and proposed that the decrease of corrosion rate is necessary conditions for the red rust appearance. As for the mechanism, El-Mahdy[7] deduced that the corrosion rate increased at the initial stage of the wet-dry cycles because the native oxide on the coating surface was dissolved into the solution and converted to hydrated zinc and aluminum oxides, and then decreased slowly owing to the accumulation of the corrosion products over the coating surface. It was not, or not obviously, in accordance with the present experimental results except for in the case of corrosion monitoring results of GL coated steel under alternate condition of 1 h-immersion in sea water and 11 h-drying as shown in Fig.6. A fact should be remembered that most of the former studies were carried out in simulated wet-drying condition involving a chloride solution. However, in natural seawater containing an amount of negative and positive ions, especially magnesium ion, situation may be changed. One common property attributed the enhanced corrosion resistance to the presence of magnesium[18-20]. Hosking[22] proposed that the oxygen reduction activity at the (zinc) cathodes was reduced by precipitation of alkali-resistant $Mg(OH)_2$, which was gradually converted to more soluble hydroxy carbonates by uptake of atmospheric carbon dioxide. This lowered the surface pH sufficiently to allow thermodynamically for general precipitation of insoluble simonkolleite ($Zn_5Cl_2(OH)_8 \cdot H_2O$) over the corroding surface thereby retarding the overall corrosion reactions. Therefore, early stage of the increase of the corrosion rate might be eliminated in the presence of magnesium, due to quenching of oxygen reduction reactions at cathodes by the formation of protective magnesium hydroxide and decreased oxygen reduction facilitating the formation of stable simonkolleite.

4. CONCLUSIONS

(1) By verification of regression statistics calculation, the Stern-Geary equation could be applied for corrosion behavior study of zinc-aluminum coated steels and the reciprocal of polarization resistance could be considered as an index of corrosion rate.

(2) The anticorrosive performance of GL coating was better than that of GF coating under same conditions, implying the amount of aluminum in galvanized steels had an influence on the corrosion resistance.

(3) Unlike simulated conditions, atmospheric corrosion in natural marine atmosphere might be a changeable and complex process subjected to the influence of elemental composition of coating materials, time of wetness(or drying period), positive and negative ions in the seawater and other parameters, which needs further study.

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