

# Corrosion Behavior of Zn and Zn-Al Alloy Coated Steels under Cyclic Wet-dry Environments

Atsushi Nishikata, Amar Prasad Yadav, Yusuke Tsutsumi,  
and Tooru Tsuru

Department of Metallurgy and Ceramics Engineering Tokyo Institute of Technology  
2-12-1, O-okayama, Meguro-Ku, Tokyo, Japan

Atmospheric corrosion behaviors of Zn, Zn-5%Al and Zn-55%Al coated steels have been investigated under cyclic wet-dry environments containing chloride ions. The wet-dry cycle was carried out by alternate exposure to immersion in 0.5 M (or 0.05 M) NaCl solutions and drying at 25 °C and 60 %RH. The polarization resistance  $R_p$  and solution resistance  $R_s$  were monitored by AC impedance technique. From the obtained  $1/R_p$  and  $1/R_s$  values, the corrosion rate of the coatings and the Time of Wetness (TOW) were estimated, respectively. Effects of chloride ions and TOW on the corrosion rates of Zn, Zn-5%Al, Zn-55%Al coatings and appearance of red rust (onset of underlying steel corrosion) under wet-dry cycles are discussed on the basis of the corrosion monitoring data.

**Keywords** : galvanized steel, Zn-5%Al, Zn-55%Al, atmospheric corrosion, Ac impedance

## 1. Introduction

Hot dip galvanized steels were widely used as construction materials because their coatings exhibit excellent protective characteristics against corrosion. The protection of the steel substrate is due to (1) the primary barrier action exhibited by the coating, (2) the secondary barrier action exhibited by the corrosion product layer, and (3) the sacrificial anodic protection exhibited by the coating on the steel substrate. There are a large number of studies on evaluation of corrosion resistance of the galvanized steels. The evaluation was usually carried out by long-term exposure test to natural environments and laboratory tests, such as salt spray test and combined cyclic corrosion tests. There are very few works on the corrosion mechanism of the galvanized steels.

In corrosion study of metals in bulk solutions, electrochemical techniques are widely employed to clarify the corrosion mechanism. Atmospheric corrosion of metals proceeds under very thin electrolyte layers. Application of electrochemical techniques to study of atmospheric corrosion was thought to be very difficult because of very limited amount of electrolytes. Nishikata *et al.* have applied the EIS to atmospheric corrosion studies.<sup>1)-6)</sup> They found that the interface of a metal and a thin electrolyte layer can be expressed by a one-dimensional transmission line (TML) circuit, and the current distribution profile over

a working electrode can be clarified using a TML model.<sup>1),6)</sup> They monitored the corrosion rates of steels<sup>1)-4)</sup> and copper<sup>1),3)</sup> under wet-dry cyclic conditions and discussed the corrosion mechanisms based on the monitoring results.

The purposes of this paper are to clarify the corrosion mechanism of Zn, Zn-5%Al, Zn-55% Al coated-steels under wet-dry cyclic environments containing chloride ions, using a electrochemical monitoring technique of atmospheric corrosion which was developed by authors before.<sup>4)</sup>

## 2. Experimental

### 2.1 Sample preparation

Three different coated-steel sheets were selected for this study, Zn-coated, Zn-5%Al alloy-coated, and Zn-55%Al alloy-coated. The thickness of the coatings was approximately 19  $\mu\text{m}$ .

A two-electrode cell arrangement was used for the impedance measurement, as shown in Fig. 1. Two metal plates were placed in an epoxy-resin holder in such a way that 10 mm x 5 mm of each plate was exposed, 0.5 mm lower than the epoxy-resin surface. This was done by attaching a 0.5mm-thick polyethylene sheet on both metal plates using a double adhesive tape during mounting in epoxy. Furthermore, the two metal plates were separated by 0.1 mm by using a mylar sheet. The edges of the

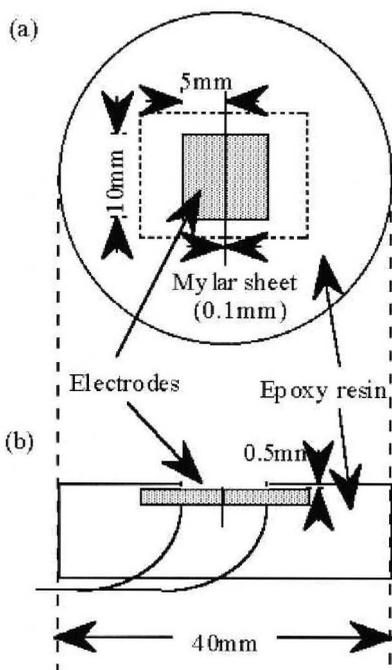


Fig. 1. Schematic diagram of a two-electrode cell used in the AC impedance corrosion monitoring of coated steels: (a) top view, (b) transverse cross-sectional view.

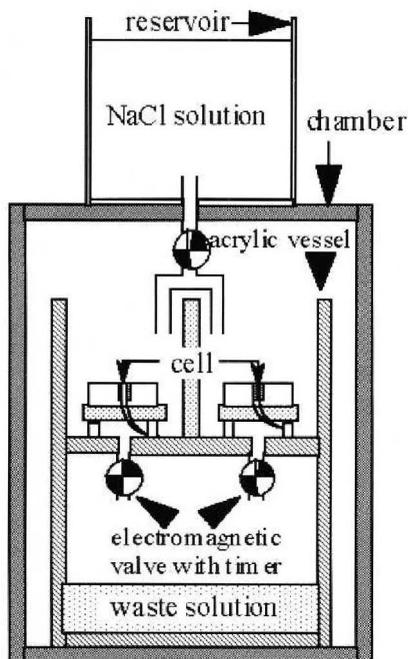


Fig. 2. Schematic of the wet-dry apparatus

exposed area and the edges separating the two metal pieces were sealed with thin layers of epoxy-resin to prevent crevice corrosion.

## 2.2 Wet-dry cycles

The wet-dry cycle was conducted by exposure to alternate conditions of 1h-immersion in a test solution and various hours of drying at 25 °C and 60%RH. NaCl solutions of 0.5 M and 0.05 M concentrations were used as the test solutions. The drying times were 3, 7 and 11h. The electrolyte layer at the onset of each dry cycle was constant (about 0.5 mm as shown in Fig. 1). The wet-dry cycle apparatus is shown in Fig. 2.

## 2.3 Corrosion monitoring

The corrosion monitoring was carried out by using an AC impedance corrosion monitor (RIKEN DENSHI CT-3) with a multiplexer controlled by a computer. The impedance at 10 mHz ( $Z_L$ ) and 10 kHz ( $Z_H$ ) was measured simultaneously, and the polarization resistance  $R_p$  was determined by subtracting  $Z_L$  from  $Z_H$ . According to the Stern-Geary equation (eq.(1)),<sup>7</sup> the corrosion current density  $i_{corr}$  can be calculated using the monitored value of  $R_p$ .

$$i_{corr} = k / R_p \tag{1}$$

where,  $k$  is a proportionality constant and is given by Tafel slopes of anodic ( $b_a$ ) and cathodic ( $b_c$ ) as follows;

$$k = -b_a b_c / 2.303 (b_a + b_c) \tag{2}$$

The  $b_a$  and  $b_c$  values for Zn in neutral chloride solutions have been reported to be 0.035 and -10 Vdecade<sup>-1</sup>, respectively.<sup>8</sup> Using these Tafel slope, the value of  $k$  was fixed at 0.015 V in this study. The total corrosion mass loss,  $\Delta M$  (gcm<sup>-2</sup>) of Zn coating was calculated by integrating the curve of  $i_{corr}$  vs. time.

The corrosion potential  $E_{corr}$  was monitored only under the immersion conditions. Furthermore, X-ray diffraction (XRD) was used to analyze the corrosion products.

## 3. Results and discussion

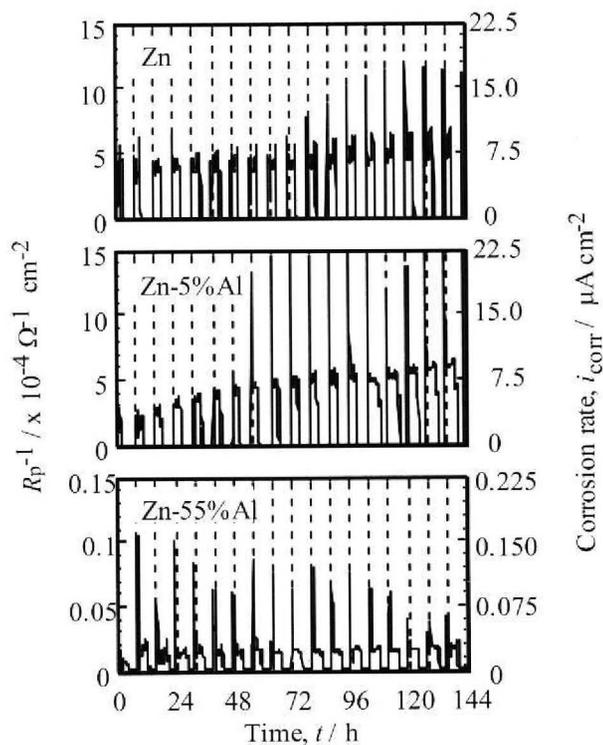
### 3.1 Time of wetness (TOW)

In this study, the solution conductance  $1/R_s$  of the water layer on the sample surface was monitored under wet-dry cycles from high frequency impedance (10 kHz). The monitored  $1/R_s$  value depends on the thickness of the water layer and the concentration of ions present in it. When the surface dries up completely, the  $1/R_s$  value becomes zero. The  $1/R_s$  value ranges  $5 \times 10^{-3}$  to  $7 \times 10^{-3} \Omega^{-1}$  during the immersion in 0.05 M NaCl solution. Just after the removal of the bulk solution, i.e. at the onset of the drying cycle, it drops to  $2 - 3 \times 10^{-3} \Omega^{-1}$  because of the extreme

reduction of the electrolyte volume (about 0.5 mm in thickness at the starting point of the drying cycle). In the latter stage of the drying, when the water layer becomes extremely thin (maybe invisible), it rapidly changes from  $2 \times 10^{-3} \Omega^{-1}$  to almost zero because the surface dries up. Therefore, in this study, TOW is defined as the time period when the  $1/R_s$  value is greater than  $1 \times 10^{-3} \Omega^{-1}$ .

### 3.2 Corrosion rate of coatings under wet-dry cycles

Monitoring results for Zn, Zn-5%Al and Zn-55%Al coated-steels are shown in Fig. 3. These were measured under cyclic conditions of 1h-immersion in 0.5M NaCl solution and 7h-drying at 25 °C and 60%RH. In each cycle, the corrosion rate for Zn coating increases as the drying



**Fig. 3.** Corrosion monitoring results for Zn, Zn-5%Al and Zn-55%Al coated-steels exposed to alternate conditions of 1h-immersion in a 0.5 M NaCl solution and 7h-drying at 60%RH and 25°C

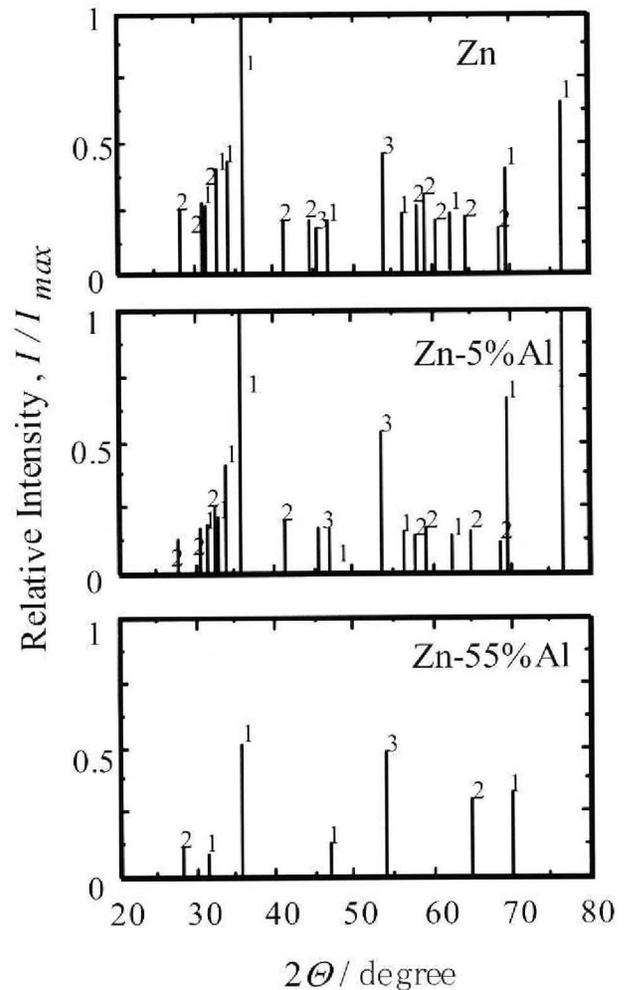
**Table 1.** The average corrosion rate  $i_{avg}$  of Zn, Zn-5%Al and Zn-55%Al coated steels after 140h-exposure to alternate conditions of 1h-immersion in 0.05M and 0.5M NaCl solution and 7h-drying at 60%RH and 25°C.

[NaCl] / M	Average corrosion rate, $i_{avr,cor}^*$ ( $\mu A cm^{-2}$ )		
	Zn	Zn-5%Al	Zn-55%Al
0.05	8.2	6.3	0.23
0.5	5.6	2.7	0.03

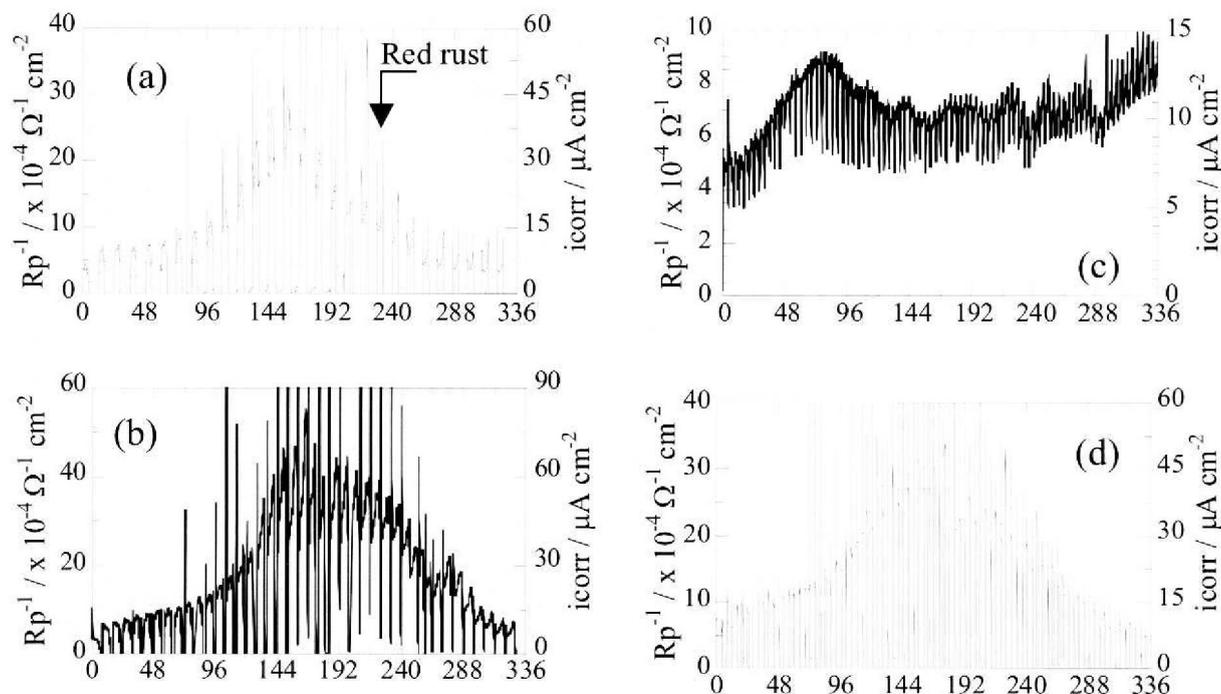
progresses. This is attributed to increase in the concentration of chloride ions due to water evaporation and enhancement of diffusion of oxygen due to decrease in thickness of water layer. Just after the surface dries up, the corrosion rate rapidly decreases. In whole cycles, the corrosion rate for Zn and Zn-5%Al is slightly accelerated by wet-dry cycles, while that for Zn-55%Al is much smaller and is not accelerated at all.

Average corrosion rates  $i_{corr}$  for Zn, Zn-5%Al and Zn-55%Al coatings are shown in Table 1.

The  $i_{avr,cor}^*$  is average corrosion current density during the coating surface is wet. The  $i_{avr,cor}^*$  was determined as follows; the  $i_{corr}$  vs. time curve was integrated and the integrated value ( $C cm^{-2}$ ) was divided by TOW (s) obtained from the high frequency impedance. It can be



**Fig. 4.** Result of XRD for Zn, Zn-5%Al and Zn-55%Al coated steels after 140h-exposure to alternate condition of 1h-immersion in a 0.05 M NaCl solution and 7h-drying at 60%RH and 25°C. 1; ZnO, 2;  $ZnCl_2 \cdot 4Zn(OH)_2$ , 3;  $Zn_3(CO_3)_2(OH)_6$ .



**Fig. 5.** Corrosion monitoring results of Zn-coated steel under drying conditions of (a) 11h, (b) 7h, (c) 3h(horizontal) and (d) 3h(inclined) and 1h-immersion in 0.5 M NaCl solution at 25°C and 60%RH.

seen from Table 1 that the corrosion rates for the wet-dry employing 0.05 M NaCl solution is slightly larger than that for 0.5 M NaCl solution. This is due probably to the difference of oxygen solubility in both solutions. Oxygen solubility in aqueous solutions is much lower in concentrated chloride concentration.<sup>9)</sup> On the other hand, Zn-55%Al indicates a higher  $i_{avr,cor}^*$  value under 0.05 M NaCl solution than that under 0.5 M NaCl solution by one order of magnitude. This great difference can not be explained only by the difference of oxygen solubility. The reason of this is not clear at the present time but seems related to the differences in the electrochemical property and the microstructure of the corrosion products formed under solutions of different NaCl concentrations.

The XRD analysis results of the corrosion products for three coatings after 140h-exposure to wet-dry cycles employing 0.05 M NaCl solution are shown in Fig. 4. For all coatings, peaks of ZnO,  $ZnCl_2 \cdot 4Zn(OH)_2$  and  $Zn_5(CO_3)_2(OH)_6$  were observed. In the diffraction pattern for Zn-55%Al coatings, any peaks related to aluminum oxides are not detected, but excellent corrosion resistance of Zn-55%Al coating implies the presence of very thin passive films of aluminum oxides.

### 3.3 Red rust appearance

In order to investigate the mechanism of onset of the

underlying steel corrosion, the Zn-coated steel was employed for longer-term corrosion monitoring under wet-dry cycles. The corrosion monitoring results are displayed in Fig. 5. The Zn-coated steels were exposed for the time period of 334 hours to alternate condition of 1h-immersion in 0.5 M NaCl solution and (a) 11h-drying(a), 7h-drying(b), and 3h-drying(c, d) at 25°C and 60%RH. The probes of (a)-(c) in Fig. 5 were placed horizontally, with the specimen surface facing upward. Accordingly, the thickness of 0.5 M NaCl solution layer present on the electrode surface was thicker than 0.5 mm (Fig. 1) at the starting point of the drying in each cycle and the NaCl solution was concentrated as the drying progressed. The probe of (d) in Fig. 5 was set at an angle of 30° with the horizontal. At the onset of the drying, the corrosion products formed during the 1h-immersion were almost washed out and the surface quickly dried up. The corrosion rates were accelerated by wet-dry in the first half and then decreased in the second half, except for horizontal probe of 1h-immersion and 3h-drying. The TOW values of (a)-(d) in Fig. 5, which were calculated from high frequency impedance data, are shown in Table 2.

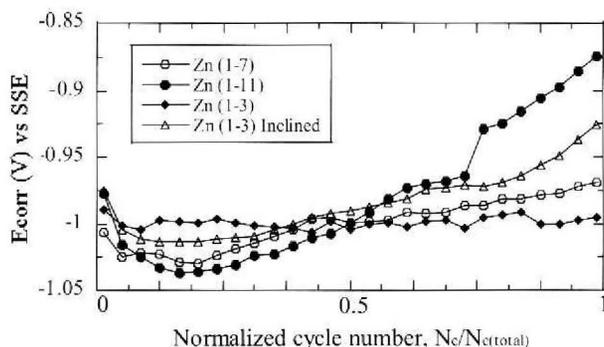
For example, under the 1h-immersion and 11h-drying, the surface was covered with continuous solution layers of NaCl for the time period of 40% (134h) of total exposure time (336h). Under 1h-immersion and 3h-drying,

**Table 2.** Summary of monitoring results of Zn-coated steel after 336h-exposure to alternate conditions of 1h-immersion in 0.5M NaCl solution and various hours of drying at 60%RH and 25°C.

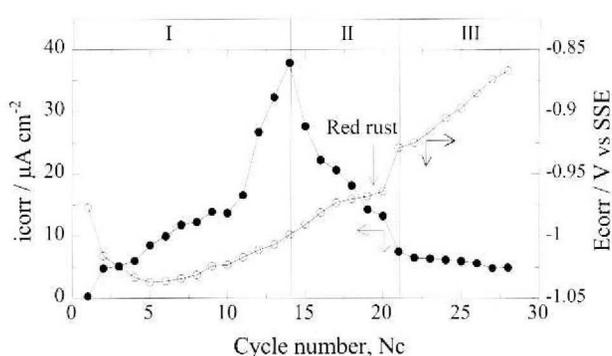
drying period (h)	cycle number	TOW (h)	$i_{avr,corr}$ ( $\mu Acm^{-2}$ )	$i^*_{avr,corr}$ ( $\mu Acm^{-2}$ )
11	28	134	7	19
7	42	264	23	29
3	84	336	10	10
3 (inclined)	84	86	4	20

the surface of horizontal probe was wet throughout experiment, meanwhile the surface of the inclined probe was wet only for 26% (86h) of the total exposure period. The average corrosion rates  $i_{avr,corr}$  and  $i^*_{avr,corr}$  are shown in third and fourth columns of Table 2, respectively. They were obtained from integration of  $i_{corr}$  vs. time of Fig. 5. The  $i_{avr,corr}$  is average corrosion rate during total exposure period (336h) and the  $i^*_{avr,corr}$  is during the probe surface was wet (TOW), respectively. If compared the average corrosion rate  $i^*_{avr,corr}$  in the period when the surface is wet, the  $i^*_{avr,corr}$  value becomes larger, as the drying period increases. Especially, for the 3h-drying where the surface did not dry up throughout experiment, as can be seen in Fig. 5(c), the corrosion was not so much accelerated by wet-dry cycles, compared to the other three cases. On the other hand, the inclined probe of 3h-drying indicates the highest average corrosion rate ( $i^*_{avr,corr}$ ) among them. Accordingly, this acceleration is attributed to change of electrical and electrochemical properties of the corrosion products during the period when the surface almost dries up.

The red rust (FeOOH) appeared only under the wet-dry condition of 1h-immersion and 11h-drying (Fig. 5(a)). It was first observed with naked eyes at the cycle indicated with an arrow in Fig. 5(a). For the other specimens exposed to wet-dry cycles of 7h-drying (Fig. 5(b)) and 3h-drying (Fig. 5(c)) and 3h-drying (Fig. 5(d)), the red rust was not observed with naked eyes during the 334h-exposure. Fig. 6 shows the variation of the corrosion potential  $E_{corr}$  of Zn-coated steels with normalized cycle number. The  $E_{corr}$  was measured after half an hour immersion of specimen in each cycle using Silver-silver Chloride Electrode (SSE) as a reference electrode. In all cases, the  $E_{corr}$  shifts to less noble values at the initial stage, followed by a gradual shift in noble direction. At the final stage, the Zn-coated steel under the 1h-immersion and 11h-drying indicated the noblest corrosion potential. The noble shift of corrosion potential implies that the corrosion rate of the coating itself decreases, but the ability as sacrificial anode decreases. In Fig. 7, the  $E_{corr}$  and  $i_{corr}$



**Fig. 6.** Plots of  $E_{corr}$  of Zn-coated steel under different wet-dry Conditions.



**Fig. 7.** Plots of  $i_{corr}$  and  $E_{corr}$  vs. cyclic number  $N_c$  under the wet-dry condition of Fig. 5(a). Arrow indicates the cycle in which red rust was first observed with naked eyes.

under 1h-immersion and 11h-drying are plotted with respect to cycle number  $N_c$ . Both data obtained after half an hour of immersion are plotted here. The corrosion rate increases with cycle number at the region I, shifting the  $E_{corr}$  to noble values. From the change of  $E_{corr}$  and  $i_{corr}$ , this acceleration was found to be due to enhancement of the cathodic reaction. It seems that the effective cathode area increases due to deposition of the white zinc corrosion products. In the region II, a sudden decrease in  $i_{corr}$  and a rapid shift of  $E_{corr}$  in noble direction was observed before the red rust appearance at the 20th cycle. This decrease is attributed to inhibition of anodic reaction due probably to accumulation of the zinc corrosion products (white rusts). It has been reported in previous paper<sup>(10,11)</sup> that the red rust appearance due to commencement of underlying steel corrosion occurs, although the Zn coating still remains on the steel surface, after rapid reduction of corrosion of the coating. In this study, from the fact that the red rust did not appear for the coatings under 7h-drying (Fig. 5(b)) and 3h-drying (Figs. 5(d)), although inhibition of corrosion rate was observed after 200 hours exposure, the inhibition is a necessary condition, but not a sufficient

condition. The sufficient drying period in each cycle seems to be necessary for the red rust appearance.

From the above monitoring results, the following mechanism of red rust appearance is proposed. In the region I of Fig. 7, the Zn-coating corroded locally at the defect sites which are initially present on the coating surface. In this region, since the coating surface is very active, the coating acts as a sacrificial anode to defects (cathode). In the region II, if the coating surface becomes inactive because of accumulation of thick zinc corrosion products, the ability of the coating as sacrificial anode commences to decrease. If the surface is wet throughout drying period in each cycle, a very large area around a defect acts as anode. As a result, in such a condition (3h-drying), no red rust appears, since the anode area is sufficiently large, although the coating surface is inactive. On the other hand, under wet-dry cycles with the sufficient drying period (11h-drying), the coating is exposed to invisible thin water layers for long time during drying periods. The anode area to the defects (cathode) is extremely limited under invisible water layers. The sufficient galvanic current is not supplied to the defects for cathodic protection, leading to commencement of underlying steel corrosion.

#### 4. Conclusions

From the monitoring results of corrosion rate and corrosion potential of Zn, Zn-5%Al and Zn-55%Al coated steels under wet-dry cycles containing chloride ions, the conclusions are drawn as follows;

1) Zn-55% Al coated steel indicates the most excellent corrosion resistance in all cases, due probably to formation of passive films mainly consisting of Al oxides. Zn and Zn-5%Al-coated steels show almost same corrosion resistance under wet-dry cycles employing 0.5 M NaCl solution, while Zn-5%Al coating has somewhat better than Zn

coating under 0.05 M NaCl solution.

2) The red rust appearance due to underlying steel corrosion was observed on the Zn-coated steel after the coating surface becomes inactive due to accumulation of zinc corrosion products (white rusts). The red rust was observed only under condition of 1h-immersion in 0.5 M NaCl and 11-drying at 25 °C and 60%RH. When the shorter drying periods (3h-drying and 7h-drying) were employed, the underlying steel corrosion did not occur during 334h-exposure period. In the cyclic wet-dry tests, the drying period is a very important factor for not only corrosion of coating itself, but also commencement of underlying steel corrosion.

#### References

1. A. Nishikata, S. Kumagai, and T. Tsuru, *Zairyo-to-Kankyo*, **43**, 82 (1994).
2. A. Nishikata, Y. Ichihara, and T. Tsuru, *Corros. Sci.*, **37**, 897 (1995).
3. T. Tsuru, A. Nishikata, and J. Wang, *Materials Science & Engineering*, **A198**, 161 (1995).
4. A. Nishikata, Y. Yamashita, H. Katayama, T. Tsuru, A. Usami, K. Tanabe, and H. Mabuchi, *Corros. Sci.*, **37**, 2059 (1995).
5. A. Nishikata, Y. Ichihara, and T. Tsuru, *Electrochim. Acta*, **41**, 1057 (1996).
6. R. P. Vera Cruz, A. Nishikata, and T. Tsuru, *Corros. Sci.*, **38**, 1397 (1996).
7. M. Stern and A. L. Geary, *J. Electrochem. Soc.*, **104**, 56 (1957).
8. W. Walter, *Corros. Sci.*, **32**, 1331 (1991).
9. W. Lang and R. Zander, *Ind. Eng. Chem. Fundam.*, **25**, 775 (1986).
10. G. A. El-Mahdy, A. Nishikata, and T. Tsuru, *Corros. Sci.*, **42**, 183 (2000).
11. G. A. El-Mahdy, A. Nishikata, and T. Tsuru, *Corros. Sci.*, **42**, 1509 (2000).