Cut Edge Corrosion of Painted Zn and 55%Al-Zn Coated Steels under Alternate Wetting and Drying

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Electrochemical study on cut edge corrosion of prepainted Zn coated (GI) and 55%Al-Zn coated (GL) steels has been performed in wet-dry cyclic conditions. Maximum width of delaminated polymer coating from the cut edge for GI and GL specimens was evaluated under wet-dry cyclic conditions. The cyclic tests were carried out for 1000 h by changing of relative humidity, where the salt of NaCl was deposited on the specimen every 48 h. The cut edge corrosion test under NaCl deposit indicated that the delamination of the GL specimen progresses at a higher rate than the GI. The electrochemical corrosion monitoring was also performed under condition of alternate exposure to immersion in NaCl solution and drying at 60%RH and 25 ℃. On the basis of the results of the delamination tests and electrochemical measurements, the mechanism of cut edge corrosion for GI and GL were discussed.

Keywords : cut edge, corrosion, salt spray, cyclic corrosion, GI, GL

1. Introduction

Cut edge corrosion is one of the problems in application of painted galvanized steel. The exposed substrate steel and Zn coating at cut edge might act as the cathode and anode respectively. Steel is protected by zinc coating. As the cut edge corrosion progresses, however, zinc coating is exhausted due to sacrificial protection and the paint de-laminates from the edge. Finally, red rusts which is an indication of steel corrosion appear at the edge.

The cut edge corrosion has been tested by long-term exposure test to natural atmospheres or accelerated tests such as Salt Spray Test (SST) and Cyclic Corrosion Test (CCT). The resistance is evaluated using delamination width from the edge (edge creep) or time to red rust. Nomura[1] reported that from the results of 15 yeas exposure test to a rural atmosphere, the delamination rate of prepainted 55%Al-Zn alloy coated steel was higher than that of Zn coated steel for first several years. After that, the former stopped, while the latter continued to progress at a constant rate throughout. Finally, the delamination width for Zn coating was larger than 55%Al-Zn.

We evaluated the corrosion resistance of non-painted Zn and 55%Al-Zn coated steels under cyclic condition of wet-dry using electrochemical impedance technique and proposed the degradation mechanism.[2)-13)] In this study, we have investigated cut edge corrosion of prepainted Zn and 55%Al-Zn coated steels under wet-dry condition in the presence of chloride ion and discussed the mechanism.

2. Experimental

The prepainted specimens of Zn-coated steel (GI) and 55%Al-Zn-coated steel (GL) are shown in Table 1. The non-painted GI and GL specimens were also used for a part of experiments. The topcoats of all specimens were chromate-free. Chromate (CR) and chromate-free (CF) were employed as the primer. Both coating surfaces of GI and GL were chromate-treated (45 mg/m²). The cut edge of all specimens was shear-cut into 20 mm x 20 mm. The backside of specimens was insulated.

Two different methods were employed for wet-dry cycle tests, (I) cyclic changes of relative humidity for evaluation of delamination width and (II) cyclic immersion and dry-ing for electrochemical study. In condition (I), the relative humidity was kept at 30% for 1h, raised to 95% for 1h, held at 95%, and then lowered to 30% for 1h. The temper-ature was kept at 60 ℃. The chloride salt was attached every 48 h by immersing the specimen in 5% NaCl sol-ution for 10 min. The corrosion test was carried out for 1000 h (250 cycles). The maximum delamination width

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Table 1. Metallic and polymer coatings employed in this study GI-CF, GL-CF : chromate-free-primer GI-CR, GL-CR: chromate-containing-primer

	GI	GL
Metallic coat	Zn(chromate-treated) / 18μm	Zn-55%Al(chromate-treated) / 27μm
Primer	Epoxy with and with out chromate / 3μm	Polyester with and with out chromate / 3μm
Topcoat	Polyester with out chromate / 11μm	Polyester with out chromate / 11μm

from cut edge was measured.

In condition (II) for the monitoring of corrosion potential E_{corr}, the wet-dry was carried out by exposed to alternate conditions of immersion in NaCl solution and drying at 60 % at 25 ℃. The corrosion potential was monitored only during the immersion condition. The employed solutions were 0.05 M (0.3%) NaCl for the non-painted specimens and 5% NaCl for prepainted. The time periods of wet/dry were 1h/1h for non-painted and 2h/2h for prepainted.

3. Results and discussion

3.1 Delamination of coating

The photographs of cut edge are shown in Fig. 1. As can be seen, large amounts of corrosion products, mainly zinc compounds, were formed on the coating surface of GL, compared to GI. The maximum depth of delamination from the cut edge is plotted with exposure time in Fig. 2. The paint on GL was delaminated at higher rate than GI. Chromate in the primes for GL inhibited the delamination. The delamination for GI would not change with and without chromate.

3.2 Monitoring of cut edge corrosion of non-painted steels

Non-painted GI and GL were exposed to alternate conditions of immersion in 0.05 M NaCl solution and drying at 60%RH and 25 ℃. The corrosion potential E_{corr} was monitored only in immersion. In Fig. 3, the E_{corr} measured at the end of immersion in each cycle is plotted vs. cycle

number. The GL indicated about 100 mV higher potential than the GI. In all cases, the E_{corr} shifted in noble direction with cycle number. This is attributed to formation of protective oxide film. In the initial stage, potential drop and restitution were repeated. In Fig. 4, the magnified figure is shown with reciprocal of polarization resistance R_p^{-1}.

Fig. 2. Maximum width of delamination from cut edge in wet and dry cyclic condition employing NaCl solution.

Fig. 3. Change in corrosion potential E_{corr} of nonpainted GI and GL with cycle number in wet-dry cyclic condition.

(a) GI-CF
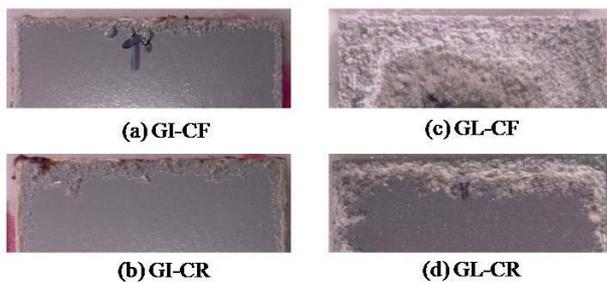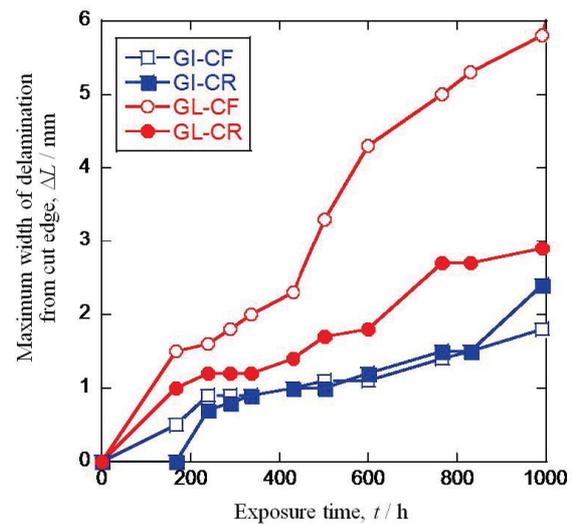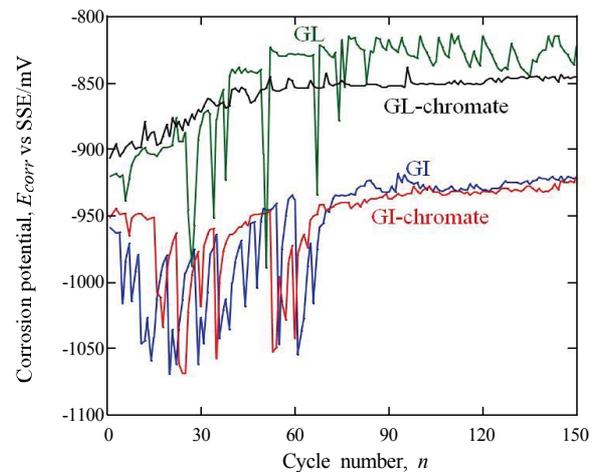
(c) GL-CF

(b) GI-CR

(d) GL-CR

Fig. 1. Photographs of cut edge corrosion of prepainted GI (Zn) and GL (Zn-55%Al) specimens with and without chromate in the primers exposed to wet and dry cyclic condition (I) employing NaCl solution for 1000 h.
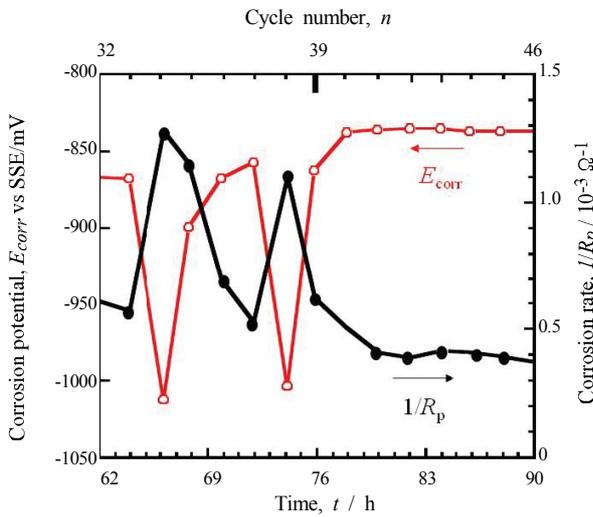
Fig. 4. Changes in corrosion potential E_{corr} and corrosion rate $1/R_p$ of non-painted GL with time in wet-dry cyclic condition.

The R_p^{-1} is an index of the corrosion rate. It can be seen in Fig. 4 that the E_{corr} shifts in less noble direction and the corrosion rate increases. This means that the potential drop is caused by breakdown of the oxide film. The potential drops more frequently took place for GI than GL and were suppressed by chromate. These results show that oxide (mainly Al_2O_3) film on GL is more stable than GI (zinc compounds) and chromate makes the oxide films more stable.

3.3 Monitoring of cut edge corrosion of prepainted steels

In previous section, the wet/dry was carried out by changing relative humidity (Figs. 1 and 2). To monitor the E_{corr}, the wet/dry was performed by cyclic immersion and drying. The numbers were 60 cycles for GI and 80 cycles for GL. After the corrosion test, red rusts were observed at the edge of GI and distinct delamination was not detected. On the other hand, for GL, whether the primer was chromate or chromate free, red rusts were not present but delamination was found at the edge, though the maximum width was decreased with chromate. Large amounts of corrosion products like those in Fig. 1(c) and (d) were not observed because the specimens were immersed in NaCl solution for longer period. The E_{corr} is plotted vs. the cycle number in Fig. 5. The E_{corr} shifts in noble direction for GI and in opposite direction for GL. The reason is discussed in next section.

3.4 Cut edge corrosion mechanism

In order to clarify dissolution behavior of the cut edge, prepainted GI and GL was corroded by immersing in 5% NaCl solution for 24 h. The photographs of the corroded
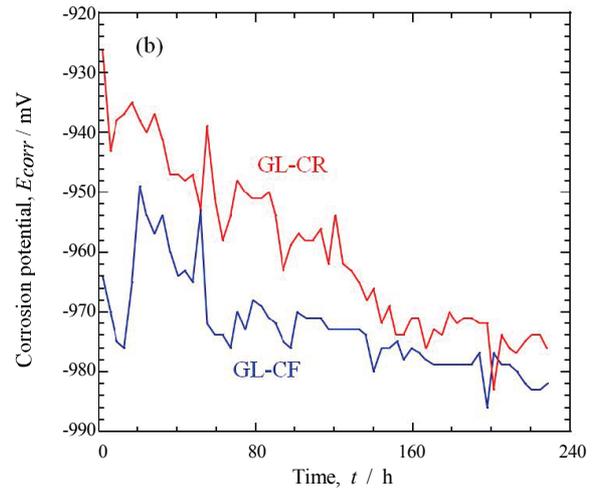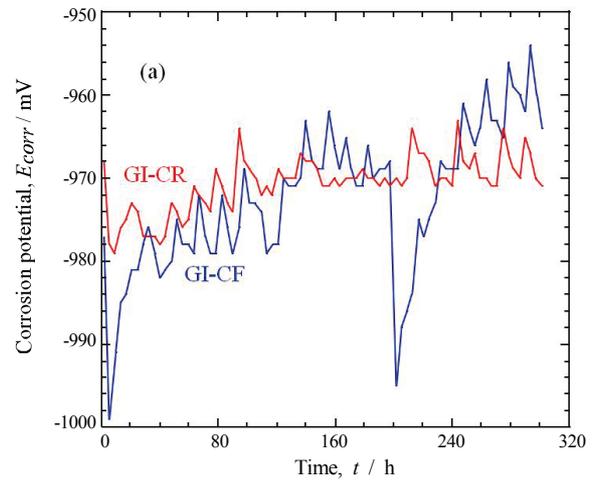

Fig. 5. Changes of corrosion potential of (a) prepainted GI-CF, GI-CR and (b) prepainted GL-CF, GL-CR exposed to alternate condition of 1h-immersion in 5%NaCl solution and 298K and 60%RH.
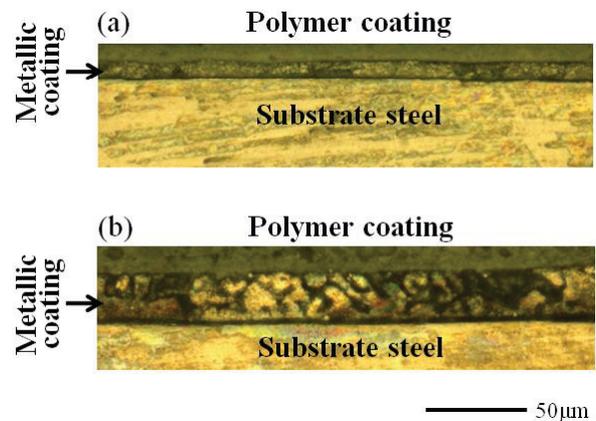

Fig. 6. Photographs of cut edge surface of metallic coating of GI and GL immersed in 5 mass% NaCl solution for 24.

cut edge are shown in Fig. 6. Since the microstructure of GI coating comprises a single phase of Zn, except for thin layers of Zn-Fe alloys at the boundary of zinc coating /substrate steel, the dissolution progresses homogeneously from the cut edge surface. On the other hand, since the microstructure of GL coating consists of two phases, Zn-rich and Al-rich phases, the Zn-rich phase dissolves selectively and the Al-rich phase passivates. As a result, as shown in Fig. 6, the Zn-rich phase disappears and Al-rich phase remains. The difference in dissolution morphology can be confirmed by the monitoring results of the E_{corr} in Fig. 5. Schematic diagrams for explaining it are shown in Fig. 7. The cut edge surface of the Zn coating layer moves backward due to corrosion. Since the coating dissolution progresses leaving little or no zinc coating layer, the ratio of steel surface (S_{Fe}) to zinc coating surface (S_{Zn}) exposed to the environment should increase as the cut edge corrosion progresses. As a result, the E_{corr} shifts in noble direction, as shown in Fig. 5(a). On the other hand, as shown in Fig. 7(b), since the corrosion of GL coating progresses leaving the Al-rich phase, the surface ratio (S_{Fe}/S_{Zn-Al}) decreases with time. This shifts the E_{corr} to less noble, as shown in Fig. 5(b).

Schematic diagrams for explaining the degradation mechanism of GI and GL are shown in Figs. 8 and 9, respectively. At the initial stage, both coatings of GI and GL corrodes by forming galvanic coupling between the substrate steel (cathode) and the coating (anode), as shown in Figs. 8(a) and 9(a). The corrosion of Zn coating (GI) progresses deeply from the cut edge (leftward in Figs. 8 and 9) at relatively slow rate, all Zn coating layer dissolving as the sacrificial anode. On the other hand, for GL, since only Zn-rich phase, which would be highly distributed on the paint side (Fig. 6), selectively corrodes, the corrosion front (coating delamination) should progress at higher rate than GI.

The corrosion of Zn coating (GI) might continue to progress at a constant rate. This can be explained as follows. As shown in Fig. 8(b), Zn coating and substrate steel are very close to each other even at the later stage. Accordingly, the coating might dissolve as the sacrificial anode even after the corrosion front is sufficiently far from the cut edge. On the other hand, in case of GL, the Zn-rich phase might be difficult to be galvanically coupled with the substrate steel at the corrosion front at the later stage, because the Al-rich phase left covers the substrate steel surface, as shown in Fig. 9(b). The Zn-rich phase at the corrosion front (anode) might form local cell with the coating (cathode) through the polymer, as shown in Fig. 9(b). In such a condition, the delamination should progress very slowly, as a report that the delamination of GL progressed
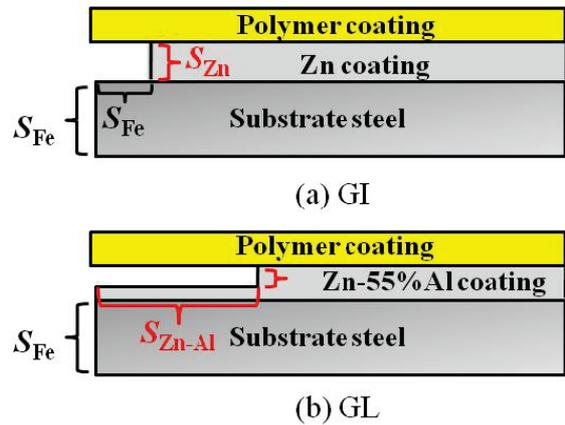

Fig. 7. Schematic diagram of exposed surfaces of hmetallic coating and substrate steel after cut edge corrosion. S_{Fe}, S_{Zn}, S_{Zn-Al} indicate the exposed surfaces of substrate steel, Zn and Zn-Al alloy coatings.
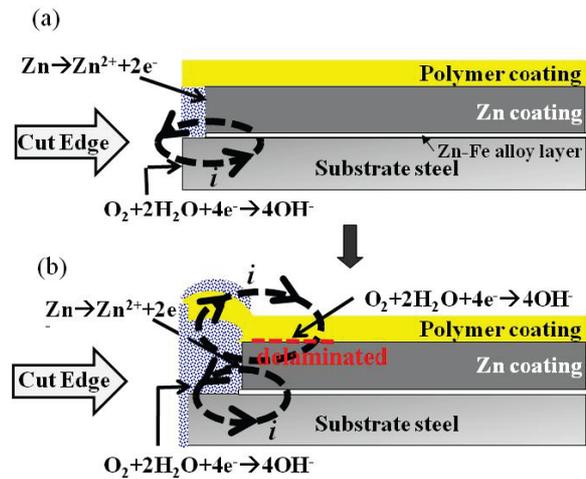

Fig. 8. Schematic drawings of cut edge corrosion of prepainted GI (a) at initial stage and (b) later stage.
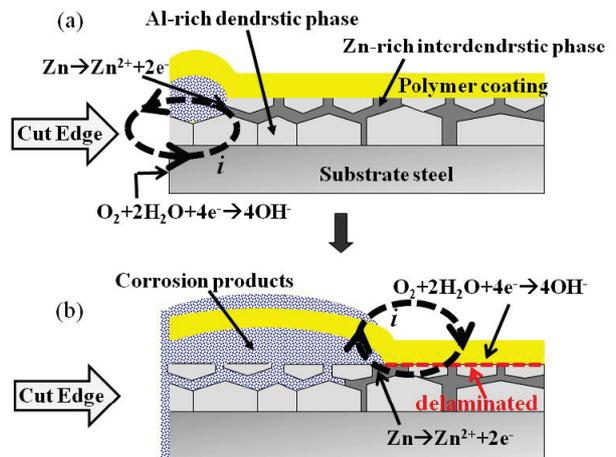

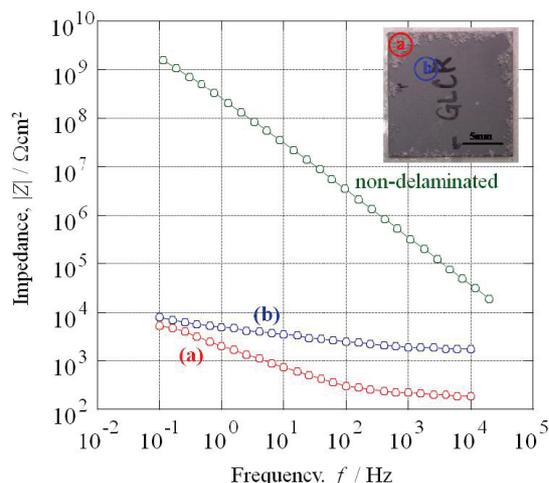**Fig. 9.** Schematic drawings of cut edge corrosion of prepainted GL (a) at initial stage and (b) later stage.

Fig. 10. Local impedance of delaminated GL-CR.

in a rural environment at higher rate than GI, but was almost ceased after several years exposure.[1] If the polymer coating is easily degraded in the environment, however, the delamination might not stop, as reported in this study. The employed wet-dry cycles might be so aggressive that the delamination of GL was not ceased. To confirm the deterioration of the polymer coating, local impedance of polymer was measured. The results are shown in Fig. 10. The EIS at non-delaminated area indicated a capacitive behavior in whole frequency region. On the other hand, local impedance at apparently sound area close to the delaminated showed much lower impedance, indicating that the local cell current can be sufficiently flowed through the polymer coating between the Zn-rich phase at the corrosion front and metallic coating surface.

4. Conclusions

The delamination width from cut edge for GI and GL under wet-dry cycles was investigated in laboratory. The delamination width of GL was larger than that for GI. This is attributed to difference of corrosion morphology of these two coatings. The degradation mechanism was proposed on the basis of the results of the accelerated corrosion test and electrochemical test.

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