Investigation of corrosion resistance of pre-painted Zn-11%Al-3%Mg-0.2%Si alloy coated steel sheet through outdoor exposure test in Okinawa

K. Ueda, A. Takahashi, Y. Kubo

Zn-11%Al-3%Mg-0.2%Si alloy coated steel sheet was well known as a coated steel exhibiting high corrosion resistance. In order to develop and enhance the cut edge corrosion resistance of chromate –free pre-painted steel sheet, the corrosion resistance of the pre-painted Zn-11%Al-3%Mg-0.2%Si alloy coated steel sheet (pre-painted SD) after 9.5 years of exposure test in Okinawa was evaluated and investigated in this study. As a result, the corrosion resistance of pre-painted SD was better than that of pre-painted Zn-0.2%Al coated steel sheet. The analysis of corrosion products of the corroded pre-painted SD by EPMA and XRD were carried out. Simonkolleite; $Zn_5(OH)_8Cl_2 \cdot H_2O$, gordaite; $NaZn_4(SO_4)Cl(OH)_6 \cdot 6H_2O$ and zinc aluminium carbonate hydroxide, $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ were found in the corrosion product under the paint film and the corrosion product of Mg-rich was observed on the steel cut edge of pre-painted SD. From these result, the mechanism of the cut edge corrosion resistance of pre-painted SD was discussed in the study.

Keywords:
Pre-painted steel sheet, Corrosion resistance, Zn-Al-Mg alloy coated steel sheet, corrosion product

INTRODUCTION

Pre-painted steel sheets are widely used for the buildings and the appliances because the paint process can be eliminated from the factory. In recent years, the development of chromate-free pre-painted steel sheets has been accelerated to protect the environment. The chromate-free pre-painted steel was first developed for the indoor appliances such as video equipment, flat panel TV etc. [1, 2] and the chromate free for the outdoor equipment was developed as a next step [3, 4]. However, there are growing needs for more enhanced corrosion resistance of chromate-free pre-painted steel sheet. The major problem of the pre-painted steel is corrosion from the cut edge because the steel itself is directly exposed to the atmosphere at the cut edge. In order to enhance the corrosion resistance from the edge, the pre-painted steel sheets have to be improved from the viewpoint of the metal coating layer, chemical conversion and primer paint.

In the field of galvanized steel sheets, the Zn-Al-Mg alloy coating that exhibit high corrosion resistance have been developed [5-15]. The Zn-11%Al-3%Mg-0.2%Si coated steel sheet (SD) is one of them and well known as high corrosion resistance material [9-11]. The corrosion mechanism of Zn-Al-Mg alloy coated steel sheet has been studied from various viewpoints. Especially, the analysis of corrosion product of Zn-Al-Mg alloy coated steel and the discussion of its effect on the corrosion resistance were reported recently. However the many reports about corrosion of Zn-Al-Mg coated steel sheet were the studies for non-painted steel sheet and there were no discussion about

corrosion from cut edge in these reports. On the other hand, in the study of pre-painted Zn-Al-Mg alloy coated steel sheet by R. P. Edavan et al [20], the high corrosion resistance (including the edge creep) of pre-painted Zn-Al-Mg alloy coated steel sheet was confirmed by SST (Salt Spray Test), CCT (Cyclic Corrosion Test) and 16 months of natural environment exposure test. The chromate and chromate-free type of pre-painted steel was tested and the same tendency between the chromate and chromate-free wasobtained. In the study by S. Yamamoto et al. [21], it was reported that the stable corrosion product containing Mg covered the cut edge of Zn-6%Al-3%Mg alloy coated steel after SST and inhibited the cathode reaction. Although the superior cut edge corrosion resistance of pre-painted Zn-Al-Mg alloy coated steel sheet examined by accelerated corrosion test and short period exposure in natural atmosphere has been reported in these study, it is required to confirm the corrosion behaviour of it by long time natural exposure and to prove the corrosion mechanism by micro-analysis of corrosion product under paint film.

The chromate-free pre-painted Zn-Al-Mg alloy coated steel sheet is expected as an eco-friendly steel product having high corrosion resistance. The main targets of this study was to evaluate the cut edge corrosion resistance of the chromate-free pre-painted Zn-11%Al-3%Mg-0.2%Si alloy coated steel sheet (pre-painted SD) after long period natural exposure test in semitropical coast district and to estimate the corrosion mechanism under the paint film near the cut edge by investigation of the corrosion products. The corrosion products were analyzed by electron probe micro analyzer (EPMA) and X-ray diffraction (XRD) in this study.

Kohei Ueda, Akira Takahashi, Yuji Kubo
Steel Research Laboratories. NIPPON STEEL CORPORATION
20-1 Futtsu, Chiba Japan 293-8511

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	Type of paint	Type of Resin	Type of Pigment	Thickness
Front side	Top Paint	High Molecular Polyester	Ivory Color Pig.	15 µm
	Primer Pint	Polyester	Chromate-Free Corrs. Resistance Pig.	5 µm
Back side	Back Paint	Polyester	Gray Color Pig.	5 µm

Table 1

EXPERIMENTAL

Sample

The Zn-0.2%Al coated steel sheet (GI) and Zn-11%Al-3%Mg-0.2%Si alloy coated steel sheet (SD) produced by CGL (Continuous hot-dip Galvanizing Line) were used as substrates. The coating weight of both types was 50 g/m^2. The chromate-free chemical conversion coating, primer paint, top and back paint as shown in Table 1 were coated on the substrate by bar-coater in the laboratory.

Outdoor exposure test

The outdoor exposure test according to JIS.Z.2381 was carried out at the exposure site in Okinawa Japan that is semitropical climate.
The site was located near the coast.
The exposure period was 9.5 years.
The exposure angle was 30 degree.
The size of samples was 50mm×100mm with downward burr (left side) and the upward burr (right side).

Measurement of corrosion width of the sample after exposure

The corrosion width (edge creep width and red rust width) at the cut edge of downward burr was measured.

Analysis of cut edge corrosion

The cross-section of corrosion site at the cut edge of exposed sample in Okinawa was observed by optical microscope and analyzed by electron probe micro analyzer (EPMA: JEOL / JXA-89-RL).
The SEM images and the element mappings were carried out. The corrosion products under the paint film near the cut edge was also observed by optical microscope after removing the paint film by tape and analyzed by and X-ray diffraction (XRD :RIGAKU / RINR1500). The analyzed area on the sample was ø 5mm in the XRD analysis.

RESULTS AND DISCUSSION

Corrosion width of pre-painted GI and SD

The photographs of samples after 9.5 years exposure in Okinawa were shown in Fig.1. The edge creep and red rust from the cut edge was largely developed on the pre-painted GI. On the other hand,the corrosion at the cut edge of pre-painted SD was only edge creep without red rust. Fig.2 shows the change of corrosion width of pre-painted GI and SD with time. There were not so much difference of the corrosion width between pre-painted GI and SD in a short period of exposure.
However, the edge creep of pre-painted GI was more developed than that of SD with time passes and there was very little red rust on the pre-painted SD. The cut edge corrosion resistance of pre-painted SD was better than that of GI in a long period of exposure.

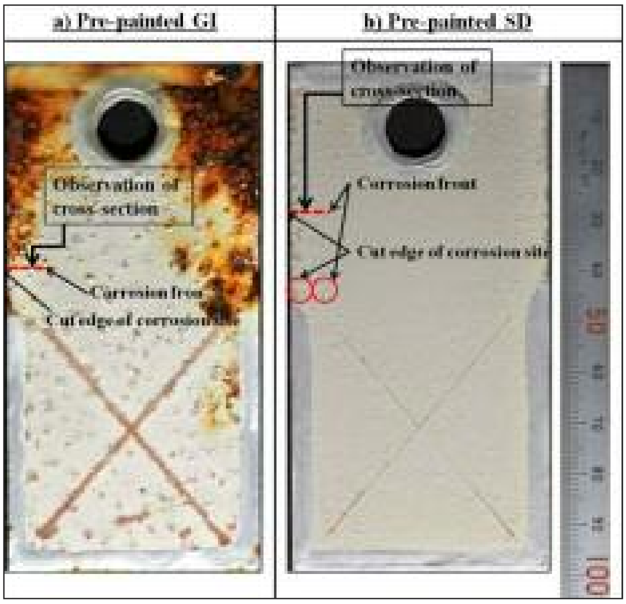

FIG. 1 ***Photographs of pre-painted GI and SD after 9.5 years of exposure test in OKINAWA Japan.***

Immagini di GI e SD preverniciati dopo test di esposizione per 9,5 anni a OKINAWA Giappone.

Cross-section analysis of the corrosion site near the cut edge

The cross-section at the red dotted line on the sample photograph shown in Fig.1 was observed and analyzed. The micro-

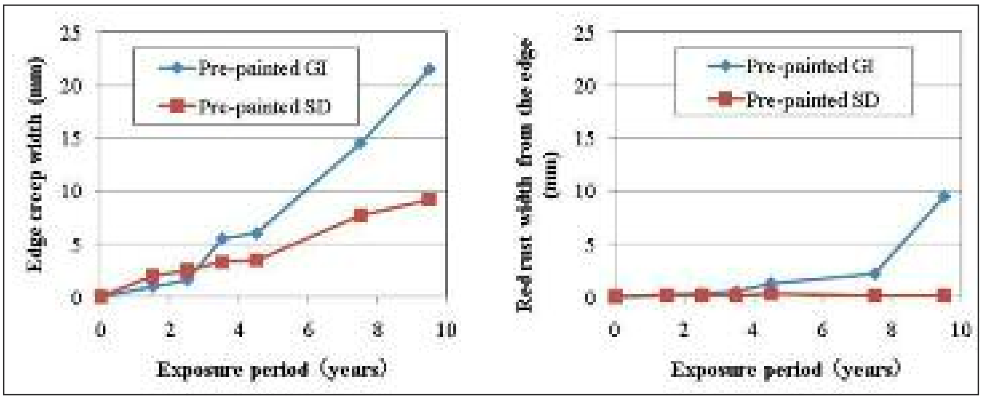

FIG.2 ***The change of corrosion width / edge creep (a) and red rust (b) of pre-painted GI and SD in OKINAWA with time.***

Evoluzione in funzione del tempo dell'entità di penetrazione della corrosione sui bordi (a) e della ruggine rossa (b) su GI e SD preverniciati nelle prove di OKINAWA

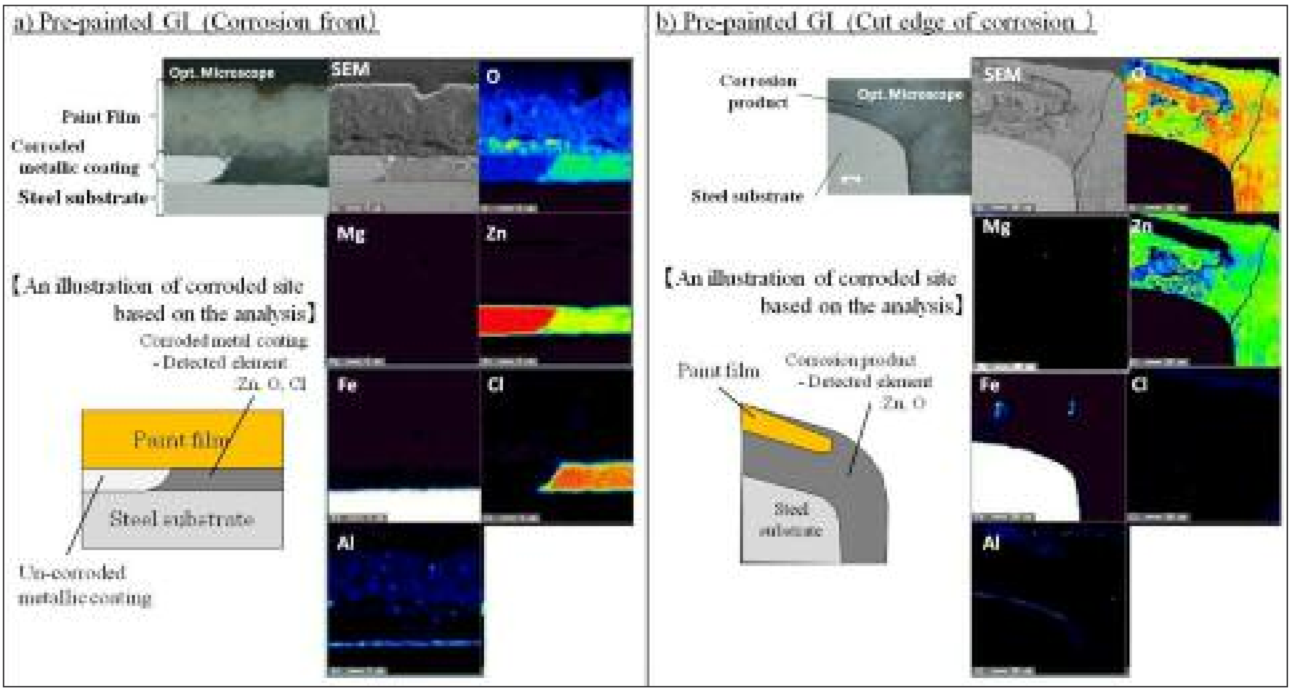

FIG. 3 ***Cross-sectional Microscope images and EPMA mappings at corrosion site of pre-painted GI after 9.5 years of exposure in OKINAKWA.***

Immagini di sezioni trasversali al microscopio e mappature EPMA nelle zone corrose di GI preverniciato dopo 9,5 anni di esposizione a OKINAKWA.

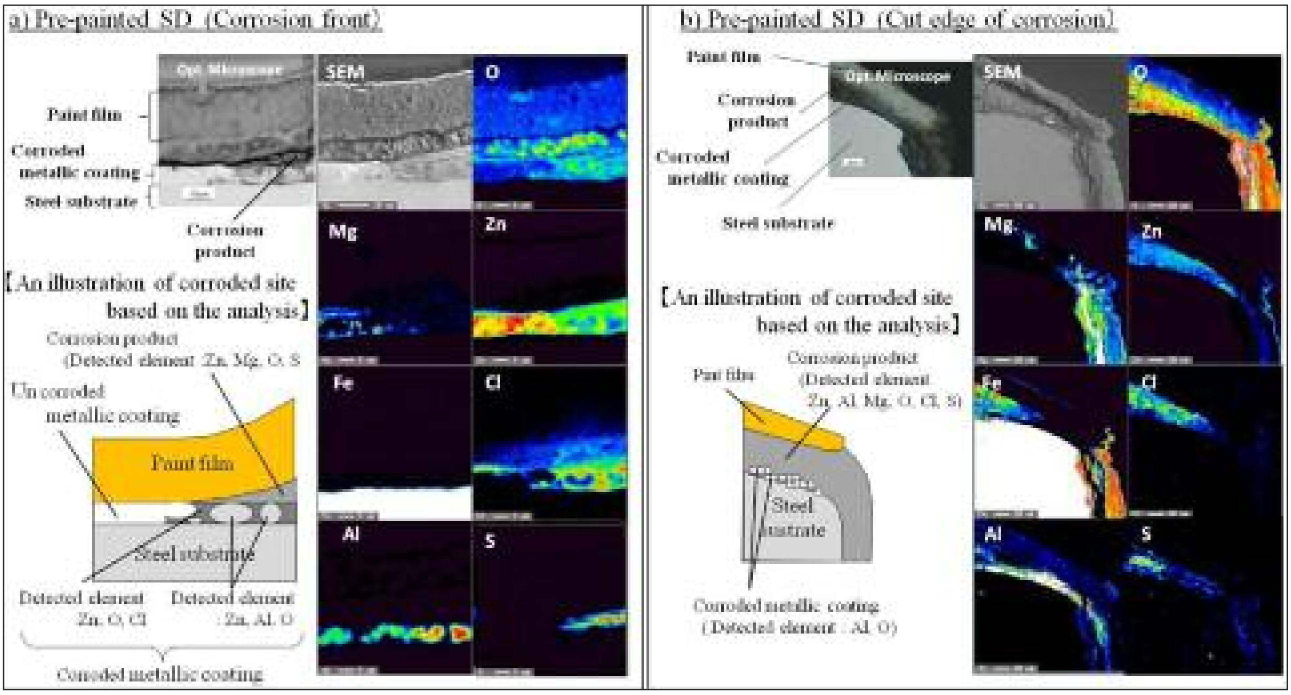

FIG. 4 ***Cross-sectional SEM image and EPMA mappings at corrosion site of pre-painted SD after 9.5 years of exposure in OKINAKWA.***

Immagini di sezioni trasversali al microscopio e mappature EPMA nelle zone corrose di SD preverniciato dopo 9,5 anni di esposizione a OKINAKWA.

scope images and EPMA mappings of pre-painted GI after 9.5years of exposure in Okinawa were shown in Fig.3.

Left side of the figure were the images of the corrosion front that was the early-phase of corrosion and the right side was the cut edge site that was the most developed phase of corrosion. In the case of pre-painted GI (Fig.3), the corroded metallic coating layer was observed under paint film at the corrosion front (Fig.3-a) and the Zn, Cl, O were detected from that site by EPMA. At the cut edge site of corrosion (Fig.3-b), the corrosion product whose volume was expanded was observed on the steel substrate and Zn, O were detected on it. In the case of GI, it is known that the zinc hydroxide $Zn(OH)_2$ is first produced as a corrosion product in the early phase of corrosion and it changes to the simonkolleite $Zn_5(OH)_8Cl_2{\cdot}H_2O$ with time and finally changed to zinc oxide ZnO. From this knowledge, the corrosion product of the corroded coating layer at corrosion front in Fig. 3 was estimated to be simonkolleite and the corrosion product at the cut edge was zinc oxide.

Fig.4 is the result of the analysis at the cross-section of the pre-painted SD after exposed in Okinawa. In the corrosion front (Fig.4-a), the expanded corrosion product was observed on the corroded metallic coating layer and the eutectic phase was first corroded in metallic coating at the corrosion front and the Al-rich phase was corroded after that. (The metallic coating layer of SD consists of an Al-rich phase and a ternary eutectic phase of Zn /Al /Zn_2Mg [9].) The elements of Zn, O ,Cl and slight amount of Mg were detected in the eutectic phase. Zn, Al, and O were detected in the Al-rich phase but the Al was more strongly detected in corroded site than that in uncorroded Al- rich phase. This result indicates the dezincification of Al-rich phase by corrosion.

The corroded Al-rich phase was remained and the stable aluminium oxide was produced on the steel substrate at the cut edge site (Fig.4-b). The elements of Zn, O, Cl, S were detected in the corrosion product on the corroded metallic coating at the corrosion front (Fig.4-a) and Zn, Al , O, Cl, S were detected in the corrosion product at the cut edge site (Fig.4-b). The element of Mg was hardly detected in both corrosion products. The zinc was preferentially dissolved from the metallic coating layer and the corrosion product of zinc was produced on the metallic coating layer near the corrosion front yet. The aluminium also dissolved from the metallic coating layer near the cut edge after progressing the corrosion and the corrosion product of zinc and aluminium was produced. Furthermore, the corrosion product of zinc and magnesium that seemed to come from metallic coating layer was observed on the exposed steel cut edge and was covered with the corrosion product at all area of the cut edge (Fig.5). This corrosion product was so stable and had been acted as protecting layer for 9.5 years in the Okinawa environment that was severe condition for corrosion.

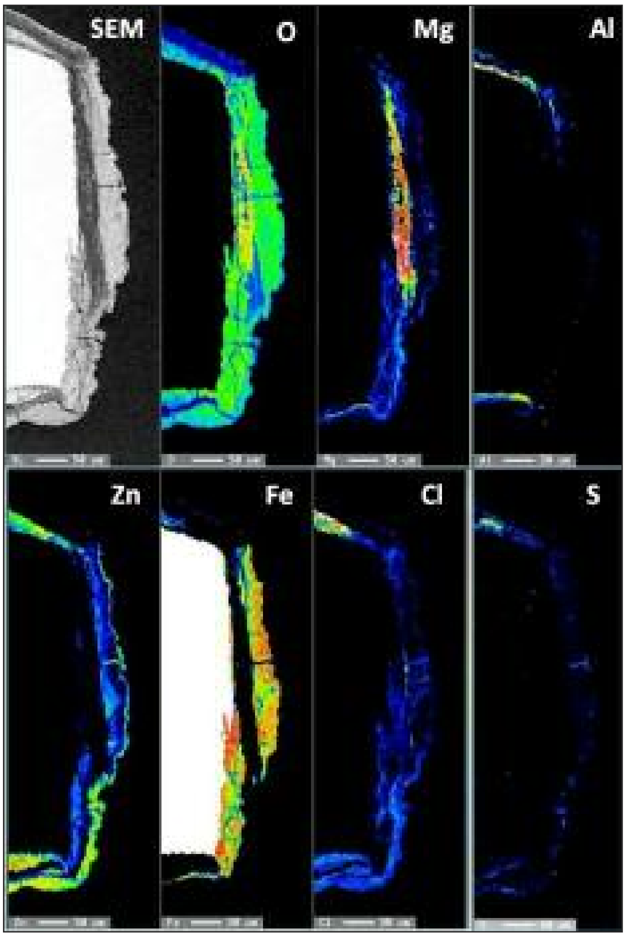

FIG. 5 ***Cross-sectional SEM image and EPMA mapping at the corroded edge of pre-painted SD after 9.5 years of exposure in OKINAKWA.***

Immagini di sezioni trasversali al SEM e mappature EPMA nei bordi corrosi di SD preverniciato dopo 9,5 anni di esposizione a OKINAKWA.

Fig.6 was a comparison of the elemental ratio of zinc, aluminium and magnesium in the selected area on the corrosion front site and the cut edge site.

The graph in Fig.6 is the calculation result from the following formulas. ZnAVG, AlAVG and MgAVG are the average detected strength of the each element in the selected area by EPMA.

[Ratio of Zn] = ZnAVG / (ZnAVG + AlAVG +MgAVG)
[Ratio of Al] = AlAVG / (ZnAVG + AlAVG +MgAVG)
[Ratio of Mg] = MgAVG / (ZnAVG + AlAVG +MgAVG)

The ratio of Zn /Al/ Mg (= 87/ 10/ 2.6) in the area A that was uncorroded metallic coating was almost corresponding to the ratio of metal composition in metallic coating layer. In the corrosion front, the Zn ratio in area B (corroded metallic coating) was lower than that in area A, but higher in area C (corrosion product) because the zinc that dissolved from the metallic coating by corrosion dissolved as corrosion product on the metallic coating. On the other hand, the ratio of Mg in area E was larger than

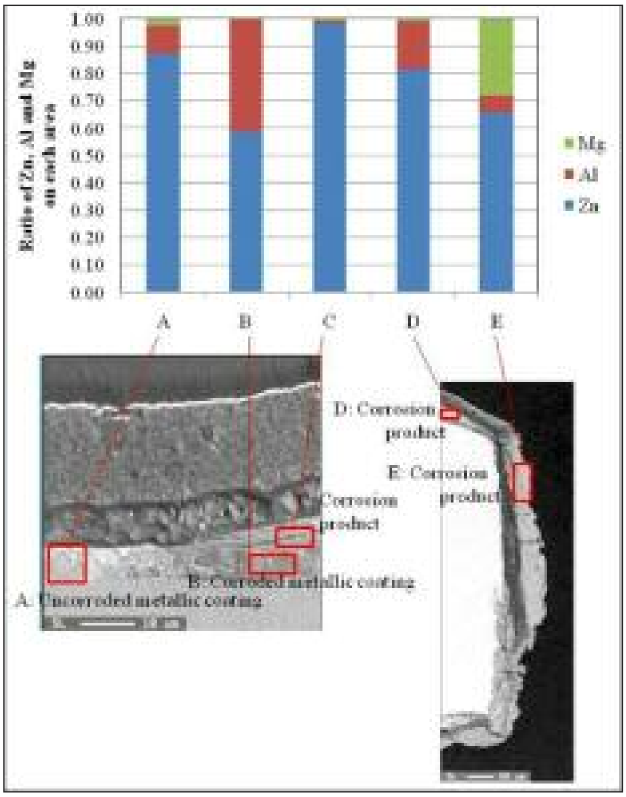

FIG. 6 ***Ratio of Zn, Al, Mg calculated from the detected strength of EPMA on each area.***

Distribuzione di Zn, Al, Mg calcolati in base ai rilevamenti dell' EPMA in ogni area.

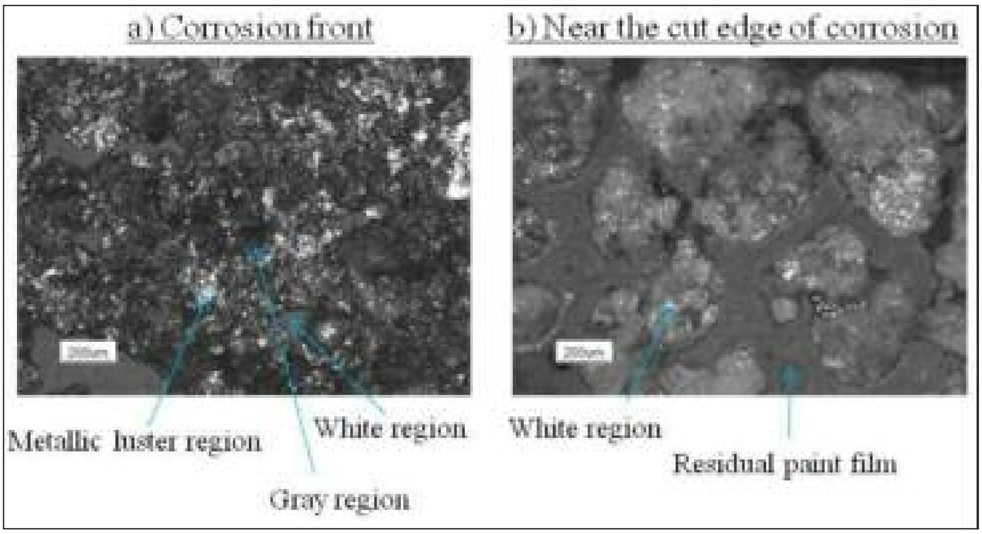

FIG. 7
Optical microscope image on the corroded metallic coating surface after removing the paint from the pre-painted SD exposed in OKINAWA (9.5 years).

Immagine al microscopio ottico della superficie corrosa del rivestimento metallico dopo rimozione della pittura da SD preverniciato esposto ad OKINAWA (9,5 anni).

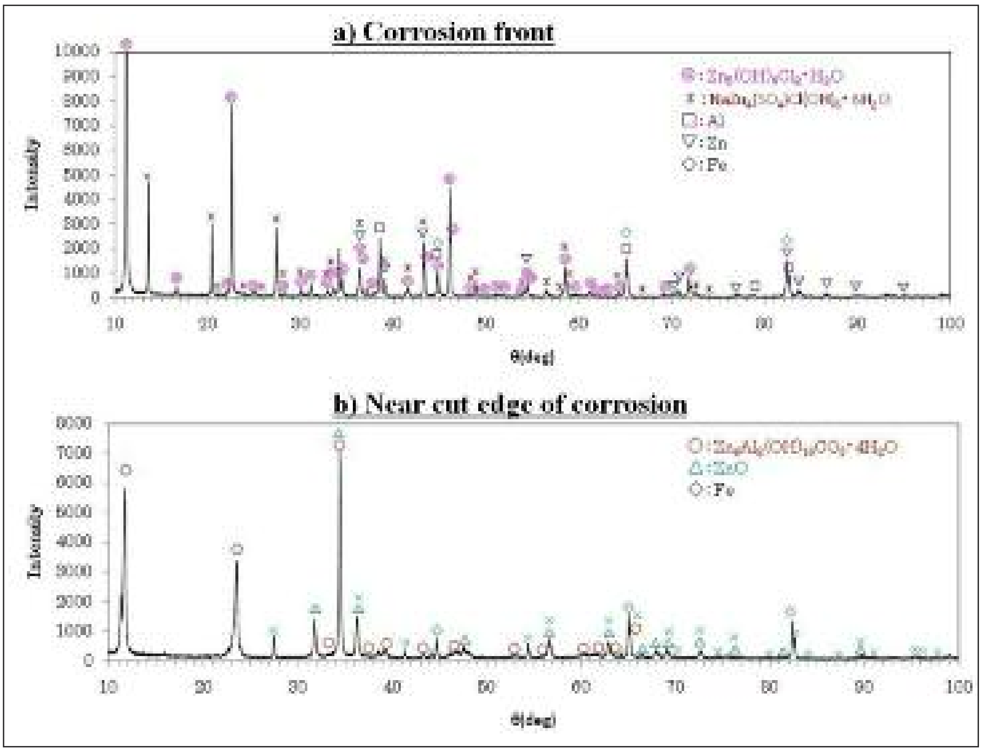

FIG. 8
X-ray diffraction diagrams of corroded metallic coating surface after removing the paint from the pre-painted SD exposed in OKINAWA (9.5 years).

Diagrammi di diffrazione ai raggi X della superficie corrosa del rivestimento metallico dopo rimozione della pittura da SD preverniciato esposto ad OKINAWA (9,5 anni).

in other area. The magnesium in metallic coating was seems to be easily dissolved by corrosion and deposited at the portion away from the corrosion front. It was considered that this behaviour was related to the pH of corrosion site under paint film and solubility of each metallic ion.

Analysis of corrosion products after removing the paint film

The paint film at the red sphere portion on the pre-painted SD sample photograph in Fig.1 was removed and the naked metallic corrosion site was observed and analyzed. The microscope images were shown in Fig.7. The white region that is corrosion product, the grey region that is corroded metallic coating and metallic lustre region that was the uncorroded metallic coating were observed at the corrosion front (Fig.7-a).

The metallic coating was covered by the island like white corrosion products near the cut edge site (Fig.7-b).

The XRD spectra of the corrosion products were shown in Fig.8. The XRD showed the presence of metallic zinc, metallic aluminium, simonkolleite, $Zn_5(OH)_8Cl_2{\cdot}H_2O$, and gordaite, $NaZn_4(SO_4)Cl(OH)_6{\cdot}6H_2O$ on the corrosion front (Fig.8-a). The metal zinc and aluminium seemed to originate from uncorroded metallic coating observed as metallic lustre region. The simonkolleite, $Zn_5(OH)_8Cl_2{\cdot}H_2O$ should be the corroded eutectic phase from the result by EPMA, while the gordaite, $NaZn_4(SO_4)Cl(OH)_6{\cdot}6H_2O$ should be metallic coating layer. The simonkolleite is well known as a stable corrosion product which is also detected in the corrosion site of Zn-Al-Mg alloy coated in the studies [17,18]. The gordaite, $NaZn_4(SO_4)Cl(OH)_6{\cdot}6H_2O$ transformed from simonkolleite under the influence of sulphate ion [19]. That is also found as a corrosion product of Zn-Al-Mg alloy coated steel after natural exposure [18]. In the case of this study, the sulphur detected by both EPMA and XRD seemed to come from marine salt because the influence of industry was small in Okinawa atmosphere.

In the result of XRD on the cut edge (Fig.8-b), the zinc aluminium carbonate hydroxide, $Zn_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$, was found. This indicated the island like corrosion product shown in Fig.7-b agrees with the corrosion product in Fig.4-b. The zinc aluminium carbonate hydroxide was also identified from the XRD and IR spectra of

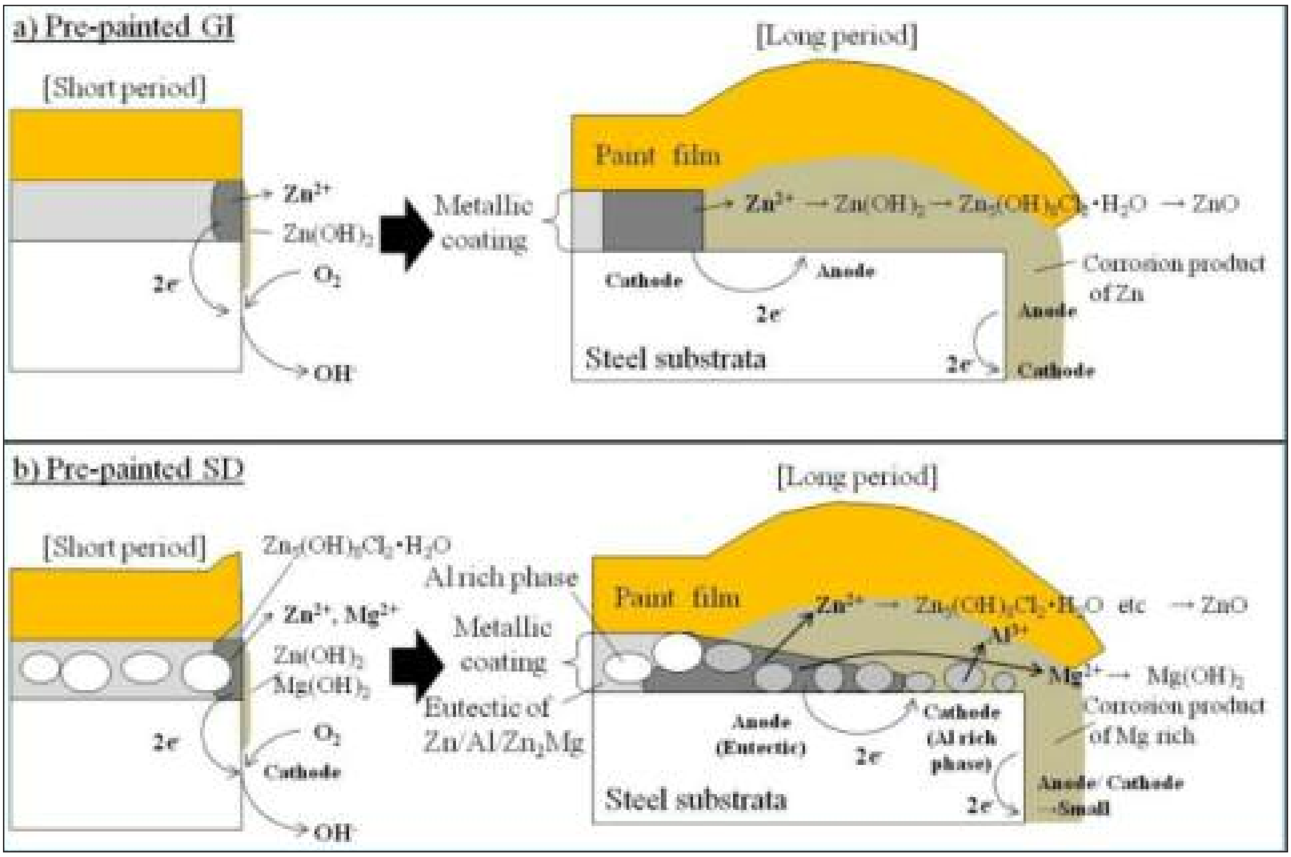

FIG. 9 ***Schematic image of cross-section of corroded pre-painted GI and SD.***
Immagine schematica della sezione trasversale di GI e SD preverniciati e corrosi.

corroded Zn-Al and Zn-Al-Mg coated steel sheets [17,18,22].
Fig.9 is the schematic images of corroded pre-painted GI and SD based on this study. In the case of pre-painted GI, the Zn2+ dissolves from Zn coating that is anodic site and deposit as a corrosion product ($Zn(OH)_2$) on the exposed cut edge in early stage of corrosion. The $Zn(OH)_2$ changes to the stable and protective corrosion product such as simonkolleite with the progress of corrosion on the cut edge. In the case of pre-painted SD, the Zn^{2+} and Mg^{2+} dissolve to the outside from the ternary eutectic phase of Zn-Al-Mg coating that is anodic site and deposit as corrosion products such as $Mg(OH)_2$ and $Zn(OH)_2$ on the exposed cut edge in early stage of corrosion. Under the paint film, the corrosion products such as simonkolleite and gordaite are produced and deposited on the corroded metallic coating in the early period. Due to those corrosion products, the edge creep was easily developed in the pre-painted SD, but this dual protective layer (corroded metallic coating layer and corrosion product layer) block the corrosion factors. The magnesium in the metallic coating layer much dissolve to the exposed cut edge with the progress of corrosion and the corrosion product of Mg-rich deposit on the exposed steel cut edge after long period. The dual corrosion product layer under the paint film and the Mg-rich layer on the exposed steel cut edge are the primary factor to enhance the edge corrosion resistance of the pre-painted SD.

CONCLUSION

The cut edge corrosion of the pre-painted GI and SD after 9.5 years exposure test in Okinawa was investigated focuses on the cut edge corrosion and the following results were obtained. Fig.9 Schematic image of cross-section of corroded pre-painted GI and SD.

- The corrosion resistance of pre-painted SD was better than that of pre-painted GI.
- The corrosion product was observed on the metallic coating layer under the paint film of pre-painted SD.
- The simonkolleite; $Zn_5(OH)_8Cl_2 \cdot H_2O$, the gordaite; $NaZn_4(SO_4)Cl(OH)_6 \cdot 6H_2O$ and the zinc aluminium carbonate hydroxide, $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ were found in the corrosion product of pre-painted SD.
- The Mg-rich corrosion product was observed on the steel cut edge of pre-painted SD.
- Producing the dual corrosion product layer under the paint film and the Mg-rich layer on the exposed steel cut edge seem to be the primary reason why the pre-painted SD exhibit the improved cut edge corrosion resistance.

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Abstract

Indagine sulla resistenza alla corrosione di lamiere di acciaio preverniciato rivestito di Zn-11% Al-3%Mg-0.2%Si mediante una campagna di esposizione in campo ad Okinawa

Parole chiave: rivestimenti – acciaio – corrosione

La lamiera di acciaio ricoperto con lega Zn-11% Al-3% Mg-0.2%Si era ben conosciuta come materiale rivestito ad alta resistenza alla corrosione. In questo studio è stata valutata e studiata la resistenza alla corrosione della lamiera d'acciaio preverniciato rivestita in lega Zn-11% Al-3% Mg-0.2%Si (preverniciato SD) dopo 9,5 anni di prova di esposizione a Okinawa, al fine di sviluppare una migliore resistenza alla corrosione sui bordi tagliati delle lamiere d'acciaio preverniciate senza cromato. La resistenza alla corrosione del preverniciato SD è risultata essere migliore rispetto a quella della lamiera di acciaio pre-verniciato rivestito di Zn-0.2% Al. Mediante EPMA e XRD, sono state effettuate analisi dei prodotti della corrosione sul preverniciato SD. Nel prodotto di corrosione sotto il film di vernice sono stati trovati simonkolleite; $Zn_5(OH)_8Cl_2 \cdot H_2O$, gordaite; $NaZn_4(SO_4)Cl(OH)_6 \cdot 6H_2O$ e idrossocarbonato di zinco e alluminio, $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ ed è stato osservato un prodotto di corrosione ricco di Mg sul bordo di taglio dell’ acciaio preverniciato SD. Partendo da questi risultati nello studio è stato discusso il meccanismo della resistenza alla corrosione del bordo di taglio preverniciato SD.