Technical Report

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Prepainted Steel Sheets Using SuperDyma™ as Base Metal

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Abstract

SuperDyma™ (SD) that is Zn-11%Al-3%Mg-0.2%Si alloy hot-dip galvanized steel sheet is well known as high corrosion resistance steel sheet. The prepainted SD also exhibited the good corrosion resistance rather than that of prepainted GI (Zn-0.2%Al coated steel sheet) in 9.5 years outdoor exposure test in Okinawa Island. Based on this experimental result, Nippon Steel & Smitomo metal Corporation developed the prepainted SD "high corrosion resistance type VIEWKOTE™".

1. Introduction

VIEWKOTE™, which serve as prepainted steel sheets for electrical appliances, is used for various applications such as the outer panels for refrigerators, washing machines, the outdoor units of air conditioners, the back panels for flat-screen TVs, etc.[1] The properties essential for the steel sheets used for outdoor devices such as the outdoor units of air conditioners are workability and long-term corrosion resistance. Previously, prepainted sheets used to be chemically treated with chromate and coated with protective paint containing chromate as the primer coating. However chromate, which contains hexavalent chromium, is an environmentally hazardous substance, prepainted sheets free of chromate were developed. For this reason, Nippon Steel & Sumitomo Metal Corporation has developed a chromate-free, prepainted sheet product that is excellent in workability and corrosion resistance, and launched it in the market under the trade name of the "high-corrosion-resistance type VIEWKOTE™".[2]

Contrary to the field of galvanized steel sheets excellent in corrosion resistance without painting, the company developed a sheet product coated with a Zn-11%Al-3%Mg-0.2%Si alloy, and under the trade name of SuperDyma™, marketed it widely for applications to electrical appliances and structures for civil engineering and building. **Figure 1** is a sectional photomicrograph of the coating layer of SuperDyma™ through a scanning electron microscope (SEM). The coating layer consists of an Al-rich phase and a ternary eutectic phase of Zn, Al, and Mg_2Zn, and is considered to be excellent in corrosion resistance.[3]

Against the above background, the team of authors started development studies for a prepainted sheet product using SuperDyma™ as the base metal, and has developed VIEWKOTE™ which is excellent in corrosion resistance and suitable for outdoor units of electric appliances. This paper presents the studies on the corrosion resistance of the said prepainted product and the characteristics of the high-corrosion-resistance type VIEWKOTE™ thus evaluated.

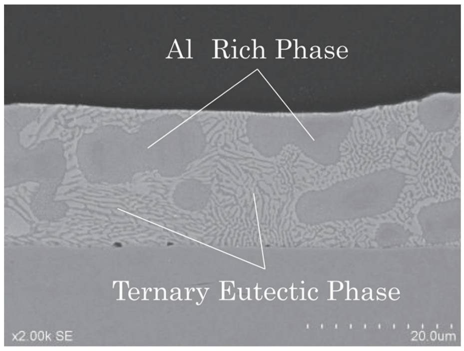

Fig. 1 Cross-sectional SEM image of SuperDyma™

2. Long-term Corrosion Resistance of Prepainted Steel Sheets Using SuperDyma™ as Base Metal [4]

Samples of SuperDyma™ and ordinary hot-dip galvanized sheets were prepared through continuous galvanizing lines (CGLs); the coating weight of both was 50 g/m^2. After chromate-free chemical treatment, they were coated on the front side with polyester primer paint containing chromate-free anti-corrosive pigment to a thickness of 5 μm, and then with high-molecular polyester top coating in ivory, 15 μm in thickness. The back sides of the sheets were coated with polyester back paint in grey with a thickness of 5 μm. The chemical treatment and paint application were done in laboratories using bar coaters (the specimens of SuperDyma™ being hereinafter referred to as the "prepainted SD" and those of ordinary hot-dip galvanized sheets as the "prepainted GI").

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The sample sheets were subjected to exposure test at a coastal location in Okinawa, Japan, for 9.5 years. **Figure 2** shows the relation between the edge creep width of the specimens and the exposure time in the left-hand graph, and the same between the red rust width and the exposure time in the right-hand graph. **Figure 3** shows the appearance examples of the specimens after the exposure for 9.5 years.

The edge creep behavior of the prepainted SD became clearly different from that of the prepainted GI after three years of exposure, and after 9.5 years, the edge creep width of the prepainted SD was only about half of that of the prepainted GI (see Fig. 2), which evidences the excellent corrosion resistance of the developed product. In addition, as seen with Fig. 3, little red rust is formed at the cut edges of the prepainted SD.

SEM sectional micrographs and element mappings by electron probe micro analyzer (EPMA) taken at a corroded cut edge of the prepainted SD are given in **Fig. 4**. As is seen in the element mapping of the corrosion front in part a), the Al-rich phase remained in the layer of corroded metallic coating, and Zn and Cl were found in the ternary eutectic phase around the Al-rich phase. On the other hand, Mg was found only in small amounts, which indicates that it had disappeared as a result of corrosion. In addition, corrosion products were deposited on the layer of the corroded metallic coating, and Zn, Cl, and S were detected in the corrosion products. Through X-ray diffraction analysis, the corrosion products at the corrosion front were found to consist Simonkolleite [$Zn_5(OH)_8Cl_2 \cdot H_2O$] and Gordaite [$NaZn_4(SO_4)Cl(OH)_6 \cdot 6H_2O$]. Thus it became clear that when the prepainted SD corroded, the Al-rich phase remained in the metallic coating layer. Corrosion products, which presumably suppressed the advancement of corrosion, formed under the paint film.

Meanwhile, near the cut edge shown in part b) of Fig. 4, corrosion products were found to deposit under the paint film; Zn, Cl, and S were detected in them. The Al-rich phase was also found to remain in

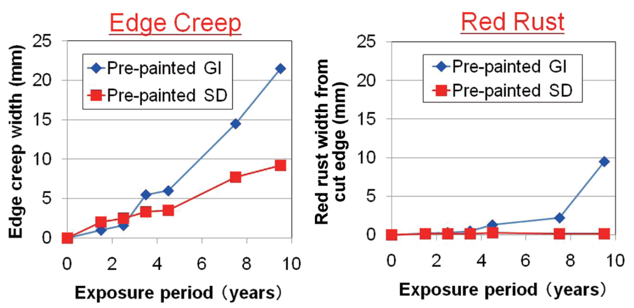

Fig. 2 Corrosion width of samples exposed in Okinawa [4)]

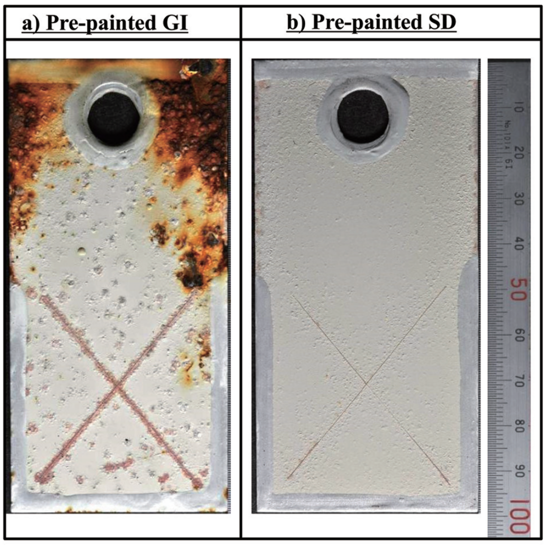

Fig. 3 Samples after 9.5y exposure in Okinawa [4)]

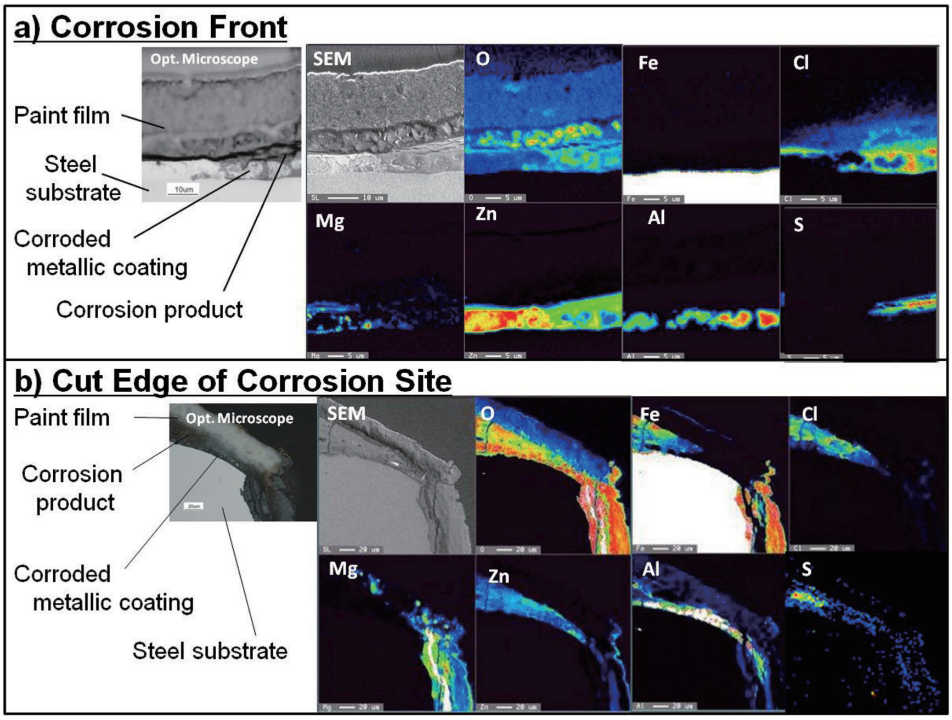

Fig. 4 Cross-sectional EPMA element mapping of prepainted SD after 9.5y exposure in Okinawa [4)]

the coating layer. In the corrosion products under the paint film near the cut edge, however, Mg was found in little quantities, but was largely detected together with O in the corrosion products on the steel substrate surface exposed at the cut edge. **Figure 5** shows EPMA mappings of an entire section of a cut edge of the same specimen. Corrosion products are found to deposit on the surface of the exposed steel substrate, and Mg was detected strongly in the corrosion products. Since Mg was not found in the corroded metallic coating layer, it is presumed that when a prepainted SD sheet corrodes, Mg is eluted from the metallic coating layer, which acts as an anode, and deposits in the form of corrosion products on the steel substrate, which acts as a cathode.

Since corrosion of prepainted steel sheets advances from cut edges, corrosion is most advanced there. The analysis of the authors showed that the Al-rich phase of the metallic coating remained under the paint films near the cut edges of the prepainted SD specimens even after an exposure of 9.5 years at the seaside in Okinawa, and corrosion products presumably resistant to corrosion progress formed around the Al-rich phase. Moreover, the cut edges of the SD specimens where the steel substrate was exposed were covered with Mg-rich corrosion products. From these findings, the corrosion mechanisms at the cut edges of the prepainted SD sheets are presumed, as shown in **Fig. 6**.

The above examination made it clear that prepainted sheets of SuperDyma™ are superior in corrosion resistance to those of ordinary hot-dip galvanized sheets (GI).

3. High-corrosion-resistance Type VIEWKOTE™ Using SuperDyma™ as Base Metal

Based on the findings described in the preceding section and using SuperDyma™ as the base metal, Nippon Steel & Sumitomo Metal has developed chromate-free, highly corrosion-resistant prepainted sheets, VIEWKOTE™ (the high-corrosion-resistance type VK, for short). **Figure 7** shows the coating structure of the developed product, and **Figs. 8** to **10** show the results of tests in which the developed VIEWKOTE™ was compared with prepainted sheets of ordinary hot-dip galvanized steel (the conventional VK, for short); all the specimens here were 0.7 mm thick, and the coating weight of the metallic layers was 40 mg/m^2. After a seven-year exposure at seaside in Okinawa, the high-corrosion-resistance type VK proved superior in terms of blister width and red rust width from cut edges and cross scratches to the conventional VK (see Fig. 8). In addition, after exposure in very wet conditions such as salt spray test for 960 h, whereas the conventional VK had blisters intensively from cut edges and cross scratches, the high-corrosion-resistance type VK had only small blisters (see Fig. 9). Moreover, as seen in Fig. 10, the high-corrosion-resistance type VK proved to have the same workability as that of the conventional VK.

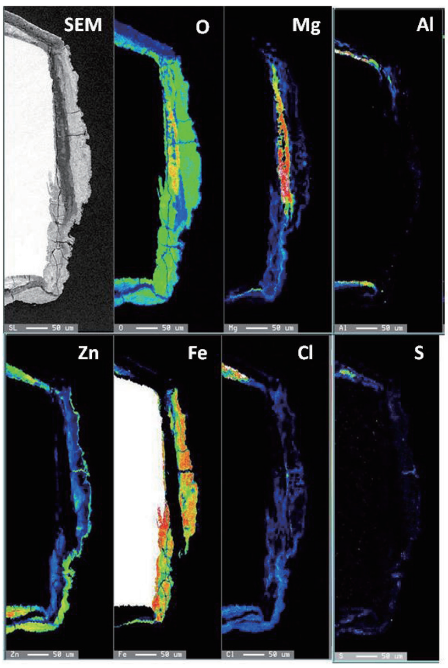

Fig. 5 Cross-sectional EPMA element mapping of prepainted SD after 9.5y exposure in Okinawa [4)]

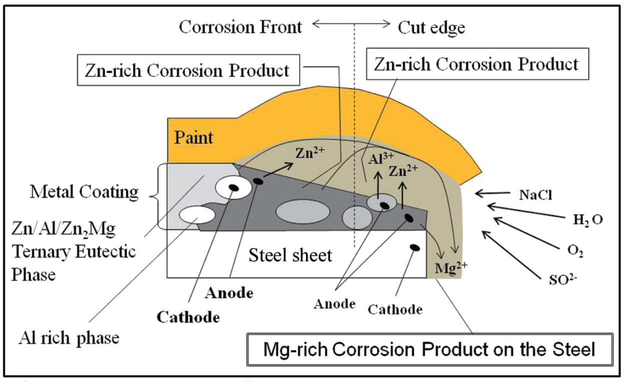

Fig. 6 Schematic illustration of estimated edge creep mechanism on prepainted SD

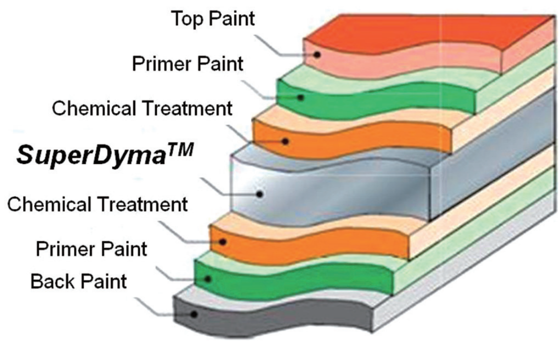

Fig. 7 Cross-sectional image of high corrosion resistance type VIEWKOTE™

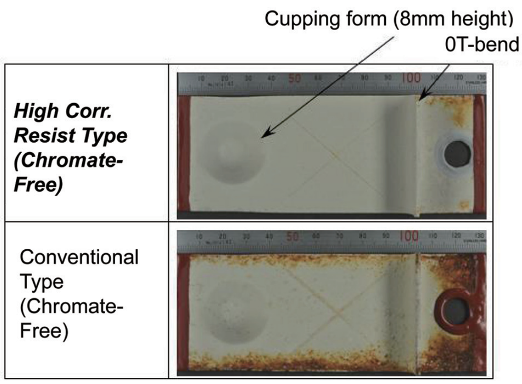

Fig. 8 VIEWKOTE™ samples after 7-year exposure in Okinawa

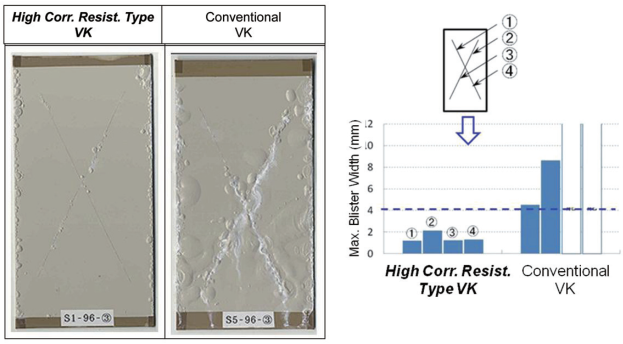

Fig. 9 VIEWKOTE™ sample photo. and data of blister width from scratch after 960-h SST

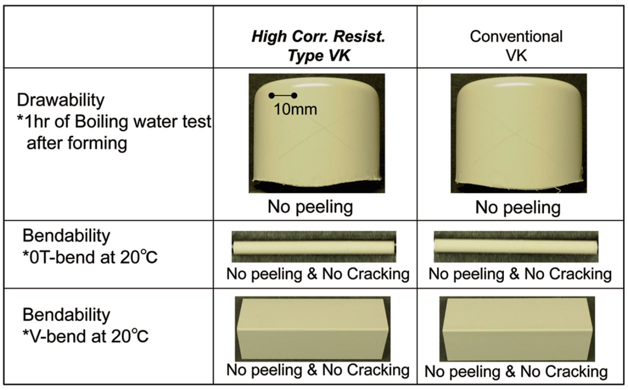

Fig. 10 Workability of VIEWKOTE™

4. Summary

The high-corrosion-resistance type VIEWKOTE™ has been developed using SuperDyma™ excellent in corrosion resistance as the base metal. The results of long-term corrosion test of the developed product and its characteristics described above can be summarized as follows:

- During the exposure test for 9.5 years at a coastal location in Okinawa, Japan, the developed type of VIEWKOTE™ exhibited excellent corrosion resistance, exceeding that of prepainted sheets using GI as the base metal.
- At a corrosion site (a cut edge, for instance) of the developed type of VIEWKOTE™, Mg and Zn were found eluted from the anodic part of the corrosion reaction, the eluted Mg formed Mg-rich corrosion products and deposited on the base metal exposed at the cut edge, which acted as a cathode, and the eluted Zn formed highly protective corrosion products (such as basic zinc chloride) under the paint films.
- The Al-rich phase in the alloy coating layer remained on the surface of the base metal even after the coating was corroded.
- The formation of chemically stable corrosion products under the paint films and on the surface of exposed base metal and the survival of the Al-rich phase in the alloy coating are presumed to be effective in suppressing the corrosion advancement, making the developed product excellent in corrosion resistance.
- The developed high-corrosion-resistance type VIEWKOTE™ using SuperDyma™ as the base metal exhibited higher corrosion resistance than and the same workability as those of conventional prepainted sheets using conventional hot-dip galvanized sheets as the base metal.

References

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