Technical Report

SuperDyma™ Crystal

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Abstract

We developed SuperDyma™ Crystal, hot dip galvanized steel sheet with an anti-counterfeiting function. SuperDyma™ Crystal is characterized by the combination of a "designed coating", on whose surface arbitrary words, etc. are formed, and "transparent blue chromate-free coating". SuperDyma™ Crystal has the same performance as conventional SuperDyma™.

1. Introduction

The hot dip galvanized steel sheet with high corrosion resistance, SuperDyma™ (Zn-11%Al-3%Mg-0.2%Si coating, hereinafter referred to as SD), has stable and excellent corrosion resistance.[1] Therefore, SD is the best choice for usage as outdoor building materials, in particular, solar panel mounts. However, in recent years, imitation SD steel sheets, which lack reliability in corrosion resistance, have been distributed in the East Asian market, and this has prompted requests from solar panel mount manufacturers to provide a means for distinguishing real SD from the imitations. Thus, Nippon Steel Corporation developed SuperDyma™ Crystal, which makes SD identifiable by combining the "designed coating", Nippon Steel's original anti-counterfeiting technology, and "clear color" (**Figs. 1** and **2**). The designed coating technology provides arbitrary designs of letters and/or patterns in a coating in the production process. Accordingly, It cannot be easily faked, unlike the conventional product marking printed on sheets with ink. The clear color technology enables the production of a blue-colored chemically treated chromate-free coating without damaging the appearance of the designed coating. This article reports the characteristics of the designed coating, and the performance of the clear color.

2. Characteristics of Designed Coating

2.1 Outline of the designed coating technology

The designed coating technology, which enables local control of the individual coating structure, creates an arbitrary design pattern that consists of an area with high glossiness (hereinafter referred to as the glossy area) and an area with weak glossiness (hereinafter referred to as the white area) (**Fig. 3**). The SD coating structure mainly consists of the dendrite primary Al, $MgZn_2$ phase, ternary eutectic structure (Zn phase/$MgZn_2$ phase/Al phase), and Mg_2Si phase.[2] With the designed coating technology, the exposure of primary Al on the surface is adjusted by controlling the formation behavior of these phases and/or structures. Namely, in the area requiring gloss, the exposure of primary Al is reduced, and in the area requiring whiteness, the exposure of primary Al is increased. As a result, the surface of the glossy area becomes slightly rough and reflects light with specular reflection, and that of the white area becomes extremely rough and reflects light with diffuse reflection. With this difference in light reflection behavior, the designed coating can be recognized visually.

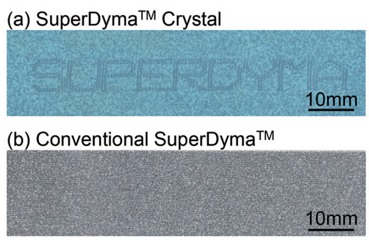

Fig. 1 Photographs of (a) SuperDyma™ Crystal and (b) conventional SuperDyma™

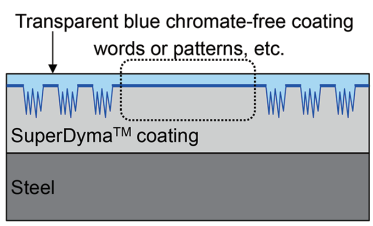

Fig. 2 Schematic cross-sectional illustration of SuperDyma™ Crystal

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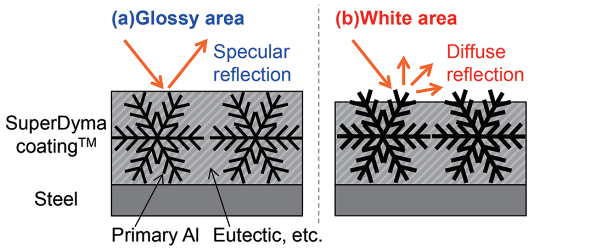

Fig. 3 Schematic cross-sectional illustrations of "glossy area" and "white area" constituting the designed coating

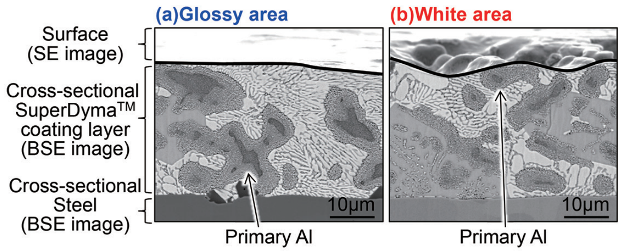

Fig. 4 Cross-sectional SEM images of "glossy area" and "white area" constituting the designed SD coating

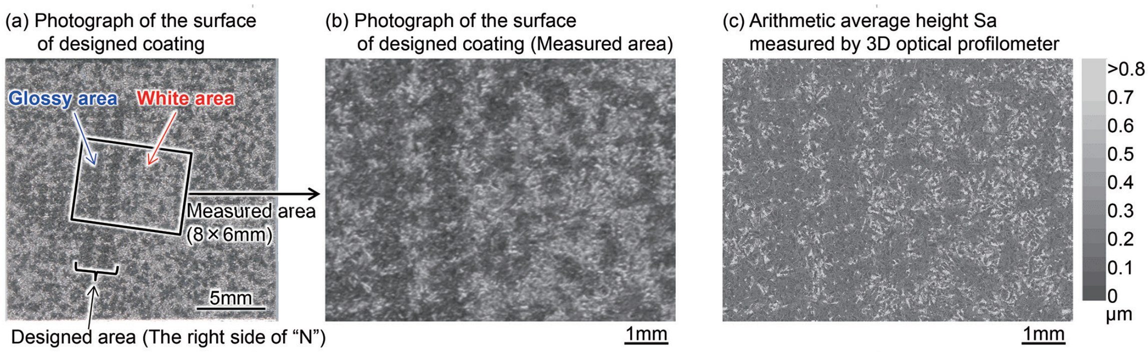

Fig. 5 Comparison between photographs of the surface of the designed coating and arithmetic average height Sa mapping image measured by a 3D optical profilometer

2.2 Result of measurement of surface state of designed coating

Hereafter, as a measurement example of the surface state of the designed coating, the result of measurement by a scanning electron microscope (hereinafter referred to as SEM) and a white light interference microscope is introduced.

As an example of the measurement by SEM, **Fig. 4** shows the cross-sectional SEM images of the glossy area and the white area after processing by a cross section polisher. In taking the cross sectional SEM image, samples were slightly inclined from the vertical posture so that the cross section state and the surface state could be simultaneously confirmed. Furthermore, for the observed area, the secondary electron image (hereinafter referred to as the SE image) and the backscattered electron image (hereinafter referred to as the BSE image) were photographed, and the photographs were synthesized respectively with the SEM image to allow easier observation of the surface roughness of the surface section (SE image) and the coating structure of the cross section (BSE image). Figure 4 confirms that the surface of the glossy area is smooth and that of the white area is rough. In addition, it is confirmed that the primary Al in the white area is exposed on the surface and therefore causes extreme roughness, while the primary Al exists in either coating structure.

Shown next is the result of the investigation on the surface state of the designed coating conducted with a white light interference microscope (3D optical profilometer, manufactured by Bruker Corporation, Contour GT I Elite). By using the height data per about 1 μm obtained by the measurement, the arithmetic average height Sa, a roughness index extending the arithmetic average roughness Ra to two dimensions, was calculated per 10 points × 10 points (about 10 μm × about 10 μm) by the expression (1) and then was mapped (**Fig. 5**).

$$\mathrm{Sa} = \sum_{x=1}^{10} \sum_{y=1}^{10} |Z_{(x,y)} - Z_{ave}| \quad (1)$$

(where $Z_{(x,y)}$ denotes the height data at the position (x, y) within the 10 points × 10 points, and Z_{ave} is the average value of the 10 points × 10 points height data.)

Figure 5 (a) shows the photograph of the appearance of the designed coating, (b) shows the same of the measured area, and (c) shows the mapped Sa image. In the photographs, it appears that the glossy area is dark and the white area is bright due to the lighting effect. The mapped Sa image shows high agreement with the photograph of the appearance. The Sa of the glossy area is mostly below 0.3 μm (smoother), and that of the white area is mainly above 0.5 μm (rougher).

From the above, it is confirmed that the surface roughness contributes to the formation of the designed coating.

3. Performance of Clear Color

3.1 JASO corrosion resistance

To investigate the corrosion resistance of clear color (the chemically treated chromate-free coating is tentatively referred to as A hereinafter), a Japan Automobile Standard Organization (JASO) Test (JASO M609-91), one of the combined cycle tests, was conducted. The upper part of the sample was flat and the lower part was an Erichsen-test cup section. The edge and the rear side were sealed with tape. As a comparison, the conventional chromate-free treated material (SD-QN)[3] and the chromate treated GI (GI-Y) were prepared. (The same comparison materials were used in the subsequent tests.) Each sample was evaluated by comparing its appearance after 30 cycles.

Figure 6 shows the result of the JASO test. In GI-Y, red rust has developed on and around the Erichsen-test cup. On the other hand, in SD-A likewise SD-QN, white rust on the flat surface is not observed, and white rust on the Erichsen-test cupped section is barely visible. From the above, it is confirmed that the corrosion resistance

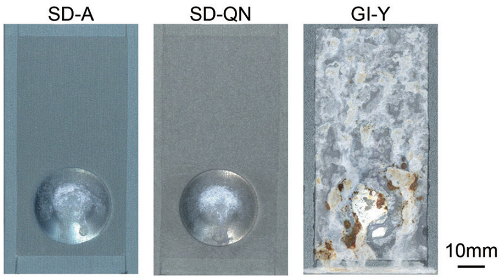

Fig. 6 Photographs of the samples after the 30 cycles of the JASO test

of SD-A is superior to that of GI-Y, and equivalent to that of SD-QN.

3.2 Exposure corrosion resistance

To investigate the color change in exposure, an exposure test was conducted at the Miyakojima exposure test and research center (Japan Weathering Test Center, 1338-1 Uenoaza-miyaguni, Miyakojima-shi, Okinawa Pref., 906-0203). Samples were exposed for durations of 1, 2, 3, and 6 months. The edges of the samples were sealed with paint, and exposed in the southward direction at an inclining angle of 45 degrees. Simultaneously, the change in appearance of the designed coating was also investigated.

Figures 7 and **8** show the result of the exposure test. The blue color remains even after the elapse of six months, while slight discoloring of SD-A is observed with time. Further, although the designed coating after six-month exposure is less visible with the normal state, it becomes obvious under the illumination of LED light.

3.3 Lubrication ability

To investigate the lubrication ability, which exerts influence on press forming, the dynamic friction coefficient of the samples was measured by using a continuous loading scratching intensity tester (manufactured by SHINTO Scientific Co., Ltd., TYPE 10), under the wet condition with coolant liquid or rust preventive oil on a surface. The dynamic friction coefficient was measured based on the sliding load obtained by sliding a steel ball of 10 mm in diameter on the surface under a load of 1.0 N and at a sliding speed of 150 mm/min.

Figure 9 shows the result of the dynamic friction coefficient measurement. Under the wet condition with coolant liquid or rust preventive oil, SD-A exhibits a similar result to those of SD-QN and GI-Y, and therefore, it is considered that there is no problem regarding the lubrication ability.

3.4 Fingerprint resistance

To investigate the fingerprint adhesive property, the samples were immersed in an artificial fingerprint liquid pursuant to JIS-K-2246 for five seconds, and the color change ΔE* before and after was measured.

Figure 10 shows the result of the measurement in the anti-fingerprint test. Although in any samples, color changes ΔE* are small, and changes in appearance are slight, SD-A exhibits the best fingerprint resistance among them.

3.5 Ethanol resistance

To investigate the influence of wiping with ethanol used to remove surface stains, a piece of gauze moistened with ethanol was attached to the sliding test machine, and the appearance of the sam-

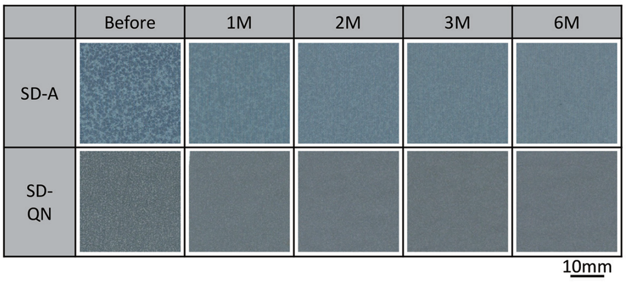

Fig. 7 Photographs of SD-A and SD-QN during the exposure test at Miyakojima, Japan, focused on color changes

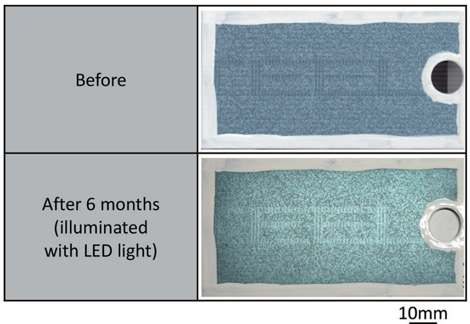

Fig. 8 Photographs of SuperDyma™ Crystal before and after the 6-month exposure test at Miyakojima, Japan, focused on an appearance change of the designed coating

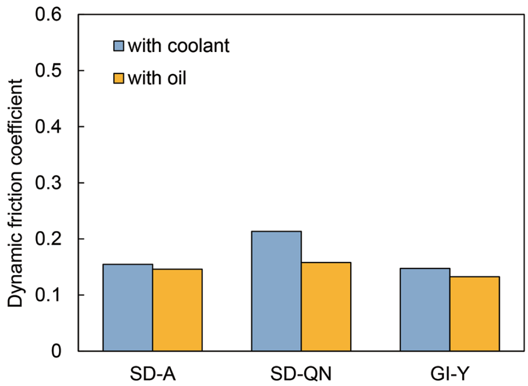

Fig. 9 Dynamic friction coefficient with coolant or oil measured by steel ball sliding test

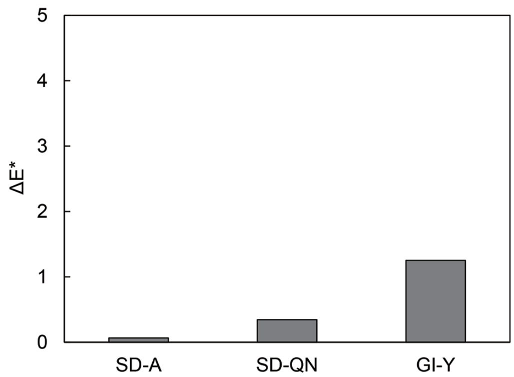

Fig. 10 ΔE* changes of samples in the anti-fingerprint test

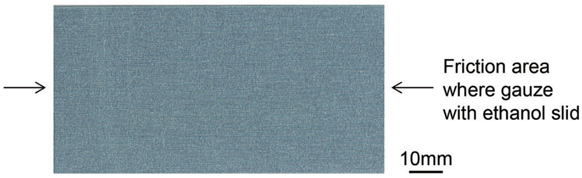

Fig. 11 Photograph of SD-A after sliding gauze with ethanol

ple was observed after twenty reciprocating sliding motions under a loading of 500 g.

Figure 11 shows the photograph of the appearance of the SD-A after the test. No change in color is observed on the sample, and good ethanol resistance is exhibited, while a slight blue stain on the gauze is visible.

4. Conclusion

We have shown that SuperDyma™ Crystal provides the original SuperDyma™ with an anti-counterfeiting function that is characterized by the “designed coating”, a distinctive anti-counterfeiting technology of Nippon Steel, and the “clear color” that improves identifiability of SD from imitation products. In the designed coating, in order to provide arbitrary designs such as letters on the coating surface, it became possible to arrange locally a glossy area having slight surface roughness and a white area having greater surface roughness. The clear color realizes the blue pigmentation in the chemically treated chromate-free coating without damaging the appearance of the designed coating. Since SuperDyma™ Crystal has a performance equivalent to that of the original SuperDyma™, it is applicable to the same conventional intended use.

References

1) Morimoto, Y. et al.: Tetsu-to-Hagané. 89 (1), 161 (2003)
2) Yamada, W. et al.: Shinnittetsu Giho. (392), 38 (2012)
3) Fuda, M. et al.: Shinnittetsu Sumikin Giho. (398), 57 (2014)

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