Technical Report

Chromate-free Galvanized Steel Sheet with Spangle Texture

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Abstract

A chromate-free galvanized steel sheet with spangle texture has been developed. The developed chromate-free galvanized iron shows the same or higher properties for corrosion resistance, friction, and welding as that of chromate. As a result, it became possible to respond to the needs of both chromate-free and spangle-finishing.

1. Introduction

Hot-dip galvanized steel sheets (often referred to as galvanized iron (GI)) are widely used in various fields of industry such as building construction, civil engineering, home appliances, office automation facilities and automobiles. They are divided roughly into two types according to surface appearance: regular spangle GI (see **Fig. 1**), in which zinc crystals present in floral patterns (spangles); and zero spangle or minimized spangle GI, in which the growth of zinc crystals is suppressed to make the spangles indiscernible to naked eye.

The regular spangle type has been used widely for the air conditioning ducts of buildings (see **Fig. 2**), and marketed characteristically for the ease of identifying the zinc plating and the efficiency in the forming of 6-foot-wide sheets into final products. In the past, the ducts were mostly installed behind the ceiling board, and were hidden from the general public. In recent years, however, the appearance effects of the spangles with random sizes, shapes and orientation have become much more valued, and there are increasing cases in which they are visible as part of the interior design of the building.

A common method of improving the corrosion resistance of spangle patterned hot-dip galvanized steel sheets was surface treatment with chromate films. Since the 2000s, however, the use of specific hazardous substances such as lead and hexavalent chromium has been restricted in Europe under the RoHS Directive, first in the field of home appliances, and environmental awareness has grown more generally in recent years. In the field of construction materials in Japan, too, the social demands for restrictions on the use of environmentally hazardous substances is increasing.

Nippon Steel Corporation considers environmental friendliness important, and has made efforts to develop an environmentally conscious product of spangled hot-dip galvanized steel sheets free of chromate. The present paper reports the characteristics of the developed product in comparison with those of conventional types treated with chromate film.

2. Design of Chromate-free Treatment Film for Hot-dip Galvanized Steel Sheet with Spangle Patterns

In the manufacture of regular spangle GI, additive elements are mixed in the plating bath by a trace amount so that they serve as the

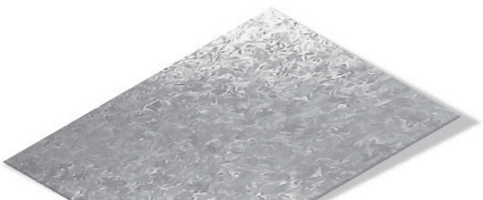

Fig. 1 Photograph of a galvanized steel sheet with spangle texture

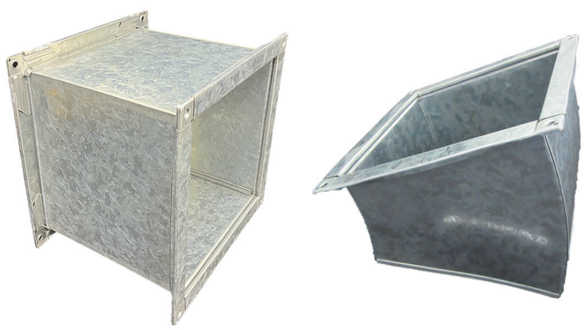

Fig. 2 Examples of duct parts made of spangled galvanized steel sheet

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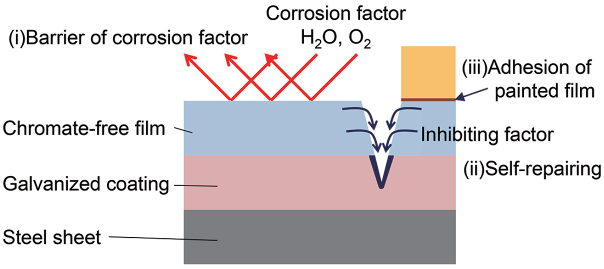

Fig. 3 Mechanism of corrosion resistant behavior of chromate-free treatment layer

nuclei for the crystallization of zinc, and zinc crystals grow from the elements to form the spangle pattern of the plating layer. On the other hand, zero spangle GI is produced usually by spraying zinc powder or water mist onto the plating surface to solidify the zinc before its crystals grow and thus reduce the size of the spangles to an invisible level.

Chromate-free treatment is applied to coat the surface of galvanized steel sheets with a special film not containing chromate. By adding corrosion inhibitors to the film having barrier effects against corrosion factors, it is possible to achieve both corrosion resistance and the freedom from chromate.[1] As a result, a corrosion resistance as high as that of conventional film containing chromate is achieved thanks to the barrier effects against corrosion factors and the self-repairing effect of inhibitors even when the zinc plating or the steel substrate is exposed owing to scratches, etc. (see **Fig. 3**). Nippon Steel designs the chemical composition of the surface treatment films for different plating alloys based on this concept.[2,3]

Since the zinc plating layer of regular spangle GI contains additive elements by trace amounts, there is inevitably a difference in electrical potential between zinc and the elements added. As a result, the zinc in the plating layer corrodes more easily than without them, and zinc rust, commonly referred to as white rust, is likely to form. However, applying conventional chromate-free treatment was insufficient to suppress the occurrence of white rust of regular spangle GI. In consideration of this, by optimally designing the compositions of the plating alloy and the chromate-free film and adequately controlling the production process in consideration of different final applications, Nippon Steel has developed a new product of spangled hot-dip galvanized steel sheets free of chromate and having the same corrosion resistance, formability and weldability as those of conventional products treated with chromate film.

3. Test Methods

Sheet of the developed spangled GI, 0.8 mm thick and having a plating weight equivalent to Z18 and coated with the chromate-free treatment film, was used as the specimen for the tests described below. The same galvanized steel sheet except that coated with conventional chemical treatment film containing chromate (chromium weight 20 mg/m^2) was used as comparative specimen.

3.1 Corrosion resistance

The salt spray test (SST) was conducted according to JIS Z 2371, and the white rust resistance was evaluated in terms of the area ratio of white rust. The edges and the back side were sealed.

In addition, an outdoor exposure test was conducted in the premises of the Kimitsu Area of Nippon Steel's East Nippon Works. Test pieces were placed horizontally without sealing the edges and the back side, and the white rust resistance was evaluated in the same way as above.

3.2 Lubricity

As an index of formability, the coefficient of dynamic friction was measured using a friction tester HEIDON-14 (made by Shinto Scientific Co., Ltd.), and the coefficient was calculated from the stress of sliding a stainless steel ball 10 mm in diameter on the specimen surface at a speed of 150 mm/min under a load of 1.0 N.

In addition to the above, to evaluate the sliding behavior of the sheets on a die press, the dynamic friction coefficient was measured also by a flat draw bead test using a precision universal testing machine AG-IS 100 kN (made by Shimadzu Corporation), wherein a flat test piece was held between flat dies of JIS SKD11, each having a contact area of 30×25 mm, at a pressing load of 0.5 kN, and pulled out. The coefficient was calculated from the load of pulling it out at a speed of 200 mm/min.

3.3 Weldability

A welding test was conducted using a servo pressure type spot welder NIDSV-35-410 (made by Dengensha Toa Co., Ltd.) and cone flat type electrodes (4.5 mm in tip diameter). Spot welding was performed by changing the welding current while two specimen sheets with the chemical treatment film were held between the electrodes in close contact with each other under a pressing load of 200 kgf. After the welding, the weld joints were observed at a cross section through an optical microscope to measure the nugget diameter, and the optimum current range for nugget formation was defined assuming that the lowest current at which the nugget diameter was $4\sqrt{t}$ or more was the lower limit, and the highest current at which the same diameter or more was obtained without causing expulsion was the upper limit.

4. Test Results

4.1 Corrosion resistance

Figures 4 and **5** show the white rust ratios of the test pieces that underwent the SST. Even after 120 hours of the test, the specimen of the developed product showed the same white rust resistance as or better than that of the comparative specimen of chromate treatment.

Figure 6 shows the result of the outdoor exposure test at Kimitsu. It is clear that the corrosion resistance of the developed product after 2 weeks of the test was the same as that of the chromate treated product.

4.2 Lubricity

Figure 7 shows the result of the sliding test using a stainless steel ball, and **Fig. 8** that of the draw bead test. In the former test, the friction coefficient of the specimen of the developed product was smaller than that of chromate treated one by roughly 0.1, evidencing a slightly better lubricity. The friction coefficients of the two types of specimens were substantially the same in the latter test.

4.3 Weldability

Figure 9 shows the measurement result of the optimum current range for nugget formation. The optimum current range of the chromate-free sheet was substantially the same as that of the chromate treated one. However, whereas the current range of the latter was 0.75 kA, the same of the former was 1.1 kA, wider than that of the comparative specimen.

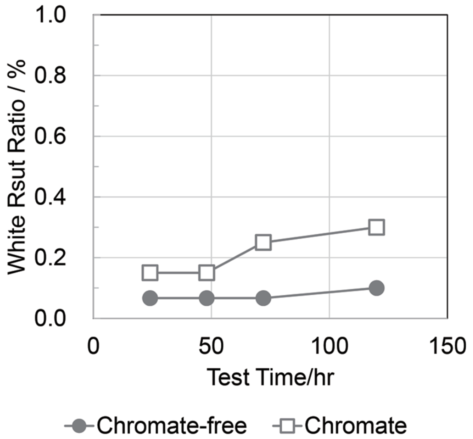

Fig. 4 Corrosion resistance of the flat specimens by salt spray test

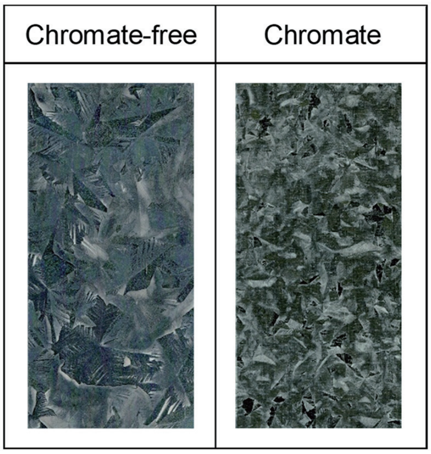

Fig. 5 Photographs of the specimens after 120 hours by salt spray test

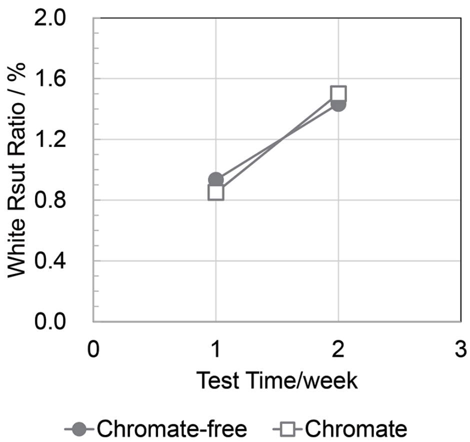

Fig. 6 Corrosion resistance of the specimens by outdoor exposure test at East Nippon Works Kimitsu Area

5. Conclusion

The present paper has described that the developed chromate-free galvanized steel sheet with spangle texture exhibits the same

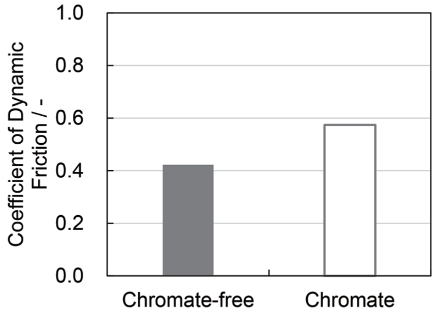

Fig. 7 Coefficient of dynamic friction by stainless steel ball sliding test

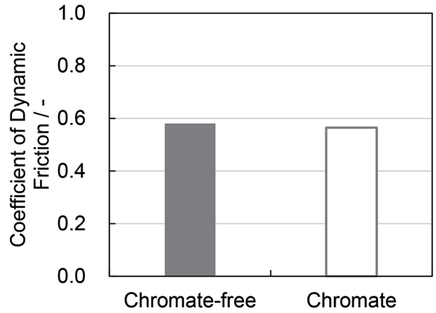

Fig. 8 Coefficient of dynamic friction by flat draw bead test

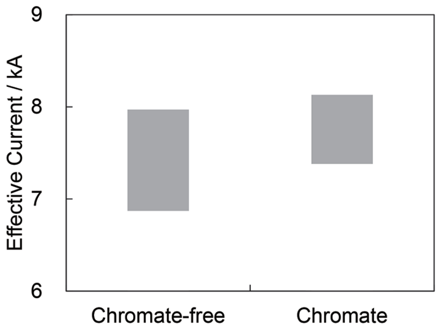

Fig. 9 Optimum current range of spot welding

corrosion resistance, lubricity and weldability as or better than those of the conventional product with surface treatment film containing chromate. This indicates that it is possible to replace the conventional galvanized steel sheets with chromate conversion treatment with the developed chromate-free sheets, which complies with environmental regulations and also meets users' preference for the appearance of regular spangles.

Nippon Steel will continue to actively advance the development of environmentally sound and high-value-added products for the market of thin sheets for building construction, thereby contributing to the creation of an environmentally friendly society.

References

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