Chromate-Free Black-Colored Steel Sheets with Excellent Heat Absorption/Radiation Property "ECO FRONTIER Z1"†

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Abstract:

"ECO FRONTIER Z1" is a chromate-free black-colored steel sheet which offers a combination of an excellent heat absorption/radiation property and EMI shielding performance in addition to an attractive black appearance and high corrosion resistance, and has earned a high evaluation as one of JFE Steel's high performance products. This steel sheet comprises a black-colored layer formed on the surface of a Zn-Ni electroplated steel sheet, and a chromate-free organic-inorganic composite film, which gives the product both excellent corrosion resistance and high heat absorption/radiation. Because "ECO FRONTIER Z1" also possesses good conductivity, spot welding can be applied. The new sheet is used in home electrical appliances, OA equipment, car audios, and other products which require groundability and EMI shielding performance.

1. Introduction

In response to heightened environmental protection activities, recent years have seen progressive moves to reduce the use of environmentally-hazardous materials[1]. Anticipating these environmental needs, JFE Steel undertook the development of various kinds of chromate-free coated steel sheets for use in home electrical appliances and OA equipment[2]. The chromate-free black-colored steel sheet introduced in this paper, "ECO FRONTIER Z1" (hereinafter referred to as Z1) is part of this chromate-free line, and has been in industrial production since 2002. Black-colored steel sheets are a type of coated steel sheet in which chromate and resin are applied to a black-colored film produced by electrochemical treatment following Zn-Ni coating. Because these sheets have an attractive jet-black appearance, have excellent corrosion resistance and designability, and also possess electrical conductivity, they are used in electrical appliances, OA equipment, and similar products. ECO FRONTIER Z1 contains no chrome and satisfies the requirements of appearance (lightness, gloss), corrosion resistance, conductivity, weldability, and resistance to cleaning and degreasing agents at the same level as conventional black-colored steel sheets in which chromate is used[3]. Furthermore, because increased heat generation accompanying higher performance in electrical appliances, OA equipment, etc. has become a problem in recent years, steel sheets with a heat radiation effect have attracted attention as one countermeasure against heat[4]. The surface film on Z1 has an excellent heat absorption/radiation property[5], making it possible to respond to needs of this type. At the same time, because Z1 possesses conductivity, it can also satisfy EMI shielding requirements. This paper describes the various properties of Z1.

2. Development Concept and Film Structure of ECO FRONTIER Z1

Figure 1 shows a cross-section of the film structure of Z1. In forming the black-colored film, JFE Steel used

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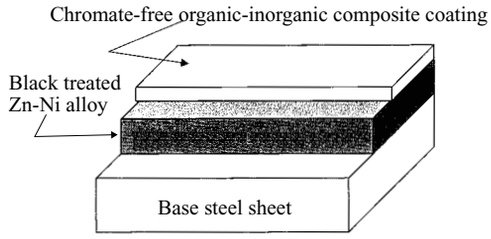

Fig. 1 The coating structure of the chromate-free black colored steel sheet “ECO FRONTIER Z1”

a method of anodic treatment of Zn-Ni electroplated steel sheets with which the company had a long record of actual results[6,7]. Next, the color is stabilized and corrosion resistance is imparted to the sheet by forming an organic-inorganic composite film 1 μm in thickness. Because the surface of the anodic-treated Zn-Ni coating is extremely active, and it is also necessary to maintain the color appearance of the product, the sheet is coated with an organic-inorganic composite treatment solution and baked after the anodic treatment in order to secure corrosion resistance, conductivity, and designability. Control of the coating weight is important, because increasing the thickness of the organic-inorganic composite film enhances corrosion resistance and designability but also reduces conductivity. To satisfy the above-mentioned requirements, a composite film consisting of a specially-designed resin and inorganic material was adopted.

3. Quality Properties

3.1 Color and Gloss

In black-colored steel sheets, the excellent design property of a low-gloss black appearance and high corrosion resistance are important features. It is therefore necessary to control the appearance properties of lightness and gloss in this type of sheet, including chromate-free products. **Photo 1** shows the appearance of Z1. For comparison, a conventional Zn electrogalvanized steel sheet (symbol: EG) and a Zn-Ni-coated sheet (symbol: Zn-Ni) have been photographed in the same field of view. From this photograph, it can be understood that Z1 has an attractive black appearance. Next, the results of a

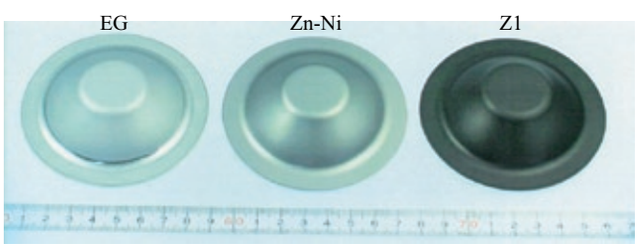

Photo 1 The “ECO FRONTIER Z1”

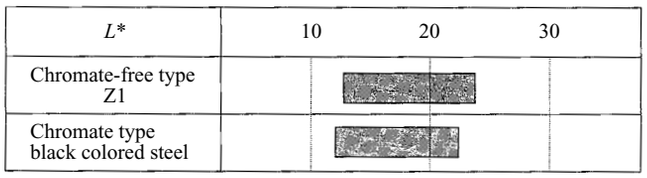

Fig. 2 L^* value of Chromate-free type “ECO FRONTIER Z1” and chromate type black colored steel

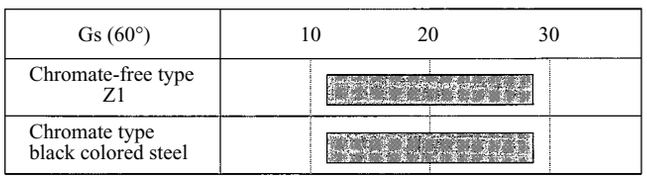

Fig. 3 Gs (60°) of chromate-free type “ECO FRONTIER Z1” and chromate type black colored steel

quantitative measurement of lightness and gloss will be presented. Using a SQ2000 color-difference meter (manufactured by Nippon Denshoku Industries Co., Ltd.), the L^* value was measured in accordance with JIS Z 8722. (The L^* value is the index of the brightness in the color system ($L^*a^*b^*$) proposed in 1976 by the Commission Internationale de l’Eclairage (CIE) as a index of lightness.) As gloss, specular gloss Gs (60°) at a specular reflection angle of 60°, as stipulated in JIS Z 8741, was measured using a VG2000 gloss meter (also manufactured by Nippon Denshoku Industries Co., Ltd.).

The results of a measurement of the L^* values of Z1 and a conventional chromate-type black-colored steel sheet are shown in **Fig. 2**, and the measured results of specular gloss Gs (60°) at a specular reflection angle of 60° are given in **Fig. 3**. It can be understood that the lightness and gloss of Z1 are both similar to those of the conventional chromate-type black-colored sheet.

3.2 Corrosion Resistance and Conductivity

The corrosion resistance of Z1 increases as the coating weight of the organic-inorganic composite film formed on the outermost surface increases. Conversely, electric conductivity is reduced as the film coating weight is increased. This relationship is shown schematically in **Fig. 4**. Corrosion resistance was evaluated as the time to 5% white rust appearance in the salt spray test (SST) as specified in JIS Z 2371. Conductivity was measured by the 4-probe method (4-probe ESP) using a Loresta-GP resistivity meter (manufactured by Mitsubishi Chemical Corp.). Assuming that conduction exists in cases where the measured value is less than 1 mΩ, conductivity was evaluated by the conduction probability when measurements were made at 10 different points. The definition of conduction probability is shown by the following Eq. (1).

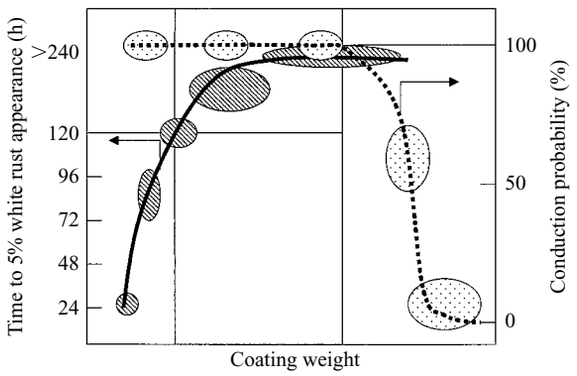

Fig. 4 Schematic diagram for the effect of coating weight on the corrosion resistance and the surface conductivity of “ECO FRONTIER Z1”

(Conduction probability (%))
= ((Number of occurrences of conduction)/10)
× 100 ····· (1)

Considering the fact that the main applications of Z1 are electrical appliances and OA equipment, the target level for corrosion resistance was set at time to 5% white rust appearance in SST ≧ 120 h. To secure adequate weldability, groundability, and EMI shielding performance, conduction probability = 100% in the above-mentioned conduction evaluation is desirable. From this viewpoint, the film was designed to be able to satisfy simultaneously the target levels for corrosion resistance and conduction, as shown in Fig. 4. Because the Zn-Ni electroplated surface which is given anodic treatment to produce a black color is extremely active, adequate corrosion resistance cannot be obtained with the chromate-free film applied to ordinary Zn-coated sheets. The authors therefore adopted a composite of an inorganic component, which is used to passivate the surface, and an organic film, which dramatically increases the barrier property against penetration by corrosive substances by enhancing the degree of crosslinking, making it possible to secure the target level. Thus, with Z1, it is possible to satisfy both corrosion resistance and conductivity requirements by controlling the coating weight of the organic-inorganic composite film within the proper range, as is shown schematically in Fig. 4.

Because Z1 possesses conductivity, as described in this section, it can be used in electrical appliances, OA equipment, car audios, and other equipment in which groundability and EMI shielding performance are required.

3.3 Spot Weldability

Because the surface film on Z1 possesses conductivity, spot welding is possible. **Figure 5** shows the relationship between the applied electrode contact force and the upper/lower welding current limits. These are the results when lapped spot welding was performed on 2

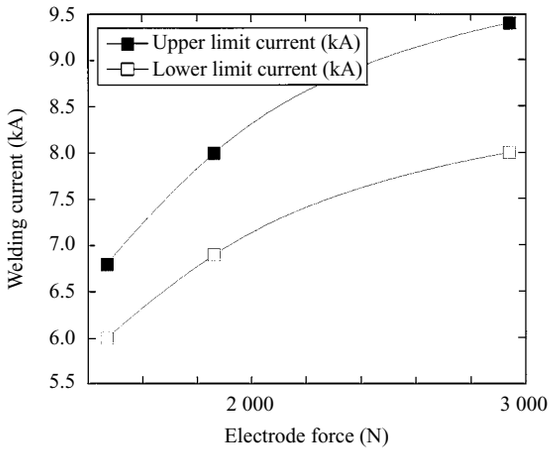

Fig. 5 Relationship between the welding current and the applied electrode contact force

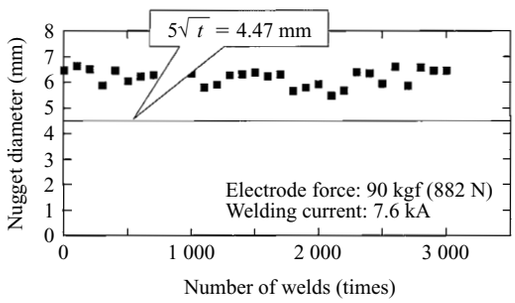

Fig. 6 Change in nugget diameter during continuous spot welding

pieces of Z1 (thickness: 0.8 mm) with a CF-type electrode (tip diameter: 5 mm) using a Type SW-608SP spot welder manufactured by Kimura Denyoki, Ltd. From these results, it can be understood that an ample appropriate welding current range exists. Furthermore, as shown in **Fig. 6**, more than 3 000 continuous spots can be welded without dressing the electrode, demonstrating that Z1 offers excellent continuous spot weldability.

3.3 Resistance to Cleaning and Degreasing Agents

Z1 is a product which is distinguished by its attractive black appearance. Therefore, in cases where the user applies press oil during forming, followed by cleaning/degreasing treatment to remove the press oil after forming, the sheet must be free of film peeling and discoloration due to the cleaning treatment. To confirm satisfactory resistance to cleaning and degreasing agents, cleaning was performed under the conditions shown in **Table 1** using CL-N364S (manufactured by Nihon Parkerizing Co., Ltd.) as a general mid-alkali degreasing agent (pH10−11) and trichloroethylene as a solvent-type degreasing agent. The condition of film peeling after cleaning was confirmed visually, and the difference in lightness L^* before and after cleaning, ΔL^*, was measured.

Table 1 Degreasing conditions

Reagents	Treating conditions
A: CL-N364S	20 g/*l*, 333 K, Dip: 3 min
B: Trichloroethylene	Vapor degreasing, 5 min

Regardless of whether cleaning was performed with the above-mentioned alkali degreasing agent or the solvent-type degreasing agent, no film peeling was observed, and the difference in lightness before and after cleaning, ΔL^*, was no more than 0.1. Thus, no significant changes in appearance were observed, confirming excellent resistance to cleaning and degreasing agents.

3.4 Heat Absorption/Radiation Property

In recent years, the increasing amount of heat generated by electrical appliances, OA equipment, and other products accompanying higher performance has become a problem. Steel sheets with a heat radiation effect have attracted attention as one countermeasure against heat[3]. The aim in this case is to reduce the internal temperature inside the equipment housing by promoting radiant heat transfer between the heat-generating source inside the equipment and the steel sheet housing by using a steel sheet with a high thermal emissivity film formed on its surface as the housing material. Formation of a paint film using a paint containing a pigment with high thermal emissivity, such as carbon black or various kinds of oxides, is considered effective for improving the thermal emissivity of the surface film. Furthermore, because the thermal emissivity of organic resins is generally high, increasing the thickness of the paint film is also effective. However, with these methods, increased surface resistance is necessarily unavoidable. On the other hand, the surface film of black-colored steel sheets has sufficient conductivity for use in parts of electrical appliances and OA equipment, as described above, and at the same time, also has a high heat absorption/radiation property.

Figure 7 is an example of an experiment which was conducted to confirm this fact. A heater was set inside a model housing made from acrylic plates 20 mm in thickness, and power was supplied by a DC stabilized power supply at a constant rate of 39 W. The internal dimensions of the model housing were 280 mm(L) × 280 mm(W) × 110 mm(H). The model housing was then set inside a thermostatic chamber in which the temperature was controlled to 23 ± 1°C, and the temperature inside the housing was measured with a thermocouple while the opening at the top of the housing was closed with either a 0.8 mm thick aluminum alloy sheet (JIS 1050), Zn electrogalvanized steel sheet, or Z1. The inner sides of the acrylic housing were covered with reflective aluminum sheets (thickness: 0.6 mm) so that exchanges of heat with the outside were mainly through

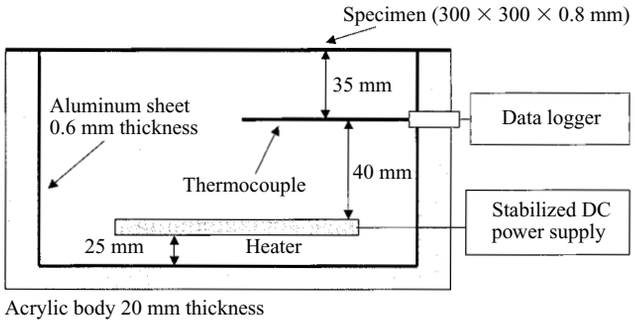

Fig. 7 Schematic diagram of apparatus used in heat radiation study

the specimen sheets placed over the opening at the top of the test apparatus. Although not shown in Fig. 7, aluminum foil was also placed directly under the thermocouple so the thermocouple would not receive radiation directly from the heater. **Figure 8** shows the change in the internal temperature of the test apparatus described above when current was supplied to the heater. The internal temperature differed remarkably depending on the type of specimen placed over the opening. As shown in Fig. 8, in comparison with aluminum alloy sheet and the EG sheet, a remarkable decrease in internal temperature was confirmed when Z1 was used.

Because the thermal conductivity of aluminum is approximately 4 times greater than that of carbon steel, there are cases where aluminum is used in the housings of personal computers and other devices where the heat radiation property is important. However, as shown by the results of this experiment, when the heat source and the equipment housing are not in direct contact, the difference in the surface film has a greater effect on the heat radiation property than that of the thermal conductivity of the metal sheet. The excellent heat absorption/radiation property of Z1 has been confirmed, and this sheet is now being used in car audio parts and others which are installed in sealed spaces and require a heat

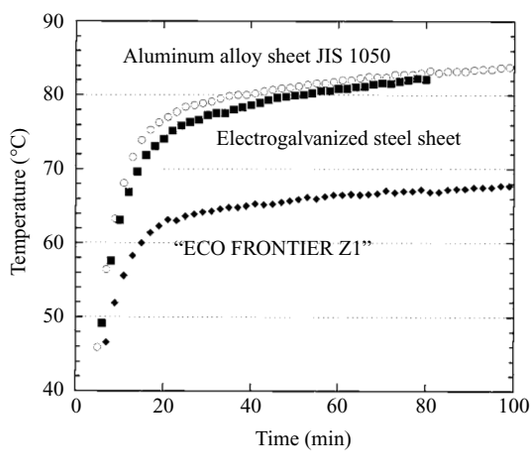

Fig. 8 Change in internal temperature of the test apparatus

absorption/radiation property.

4. Conclusion

The properties of a chromate-free black-colored steel sheet, “ECO FRONTIER Z1,” which features an organic-inorganic composite film on an anodic-treated black-colored Zn-Ni electroplated steel sheet, were presented. ECO FRONTIER Z1 has appearance, corrosion resistance, electric conductivity, and resistance to cleaning and degreasing agents equal to those of conventional black-colored steel sheets, and also possesses an excellent heat absorption/radiation property. From the viewpoint that Z1 is capable of responding to the rising environmental needs of the future, while also offering an effective countermeasure for heat generation accompanying higher performance in electrical appliances, OA equipment, and car audios, expanded application is expected.

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