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Development of Chromate-Free Coated Hot-Dip Galvanized Steel Sheet "Eco Frontier™ JM" †

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Abstract:

At a site of heating, such as a brazing portion of a heat exchange unit, discoloration of chemical treatment layer on steel sheet may interfere with the use. "Eco Frontier™ JM" is a new inorganic chromate-free coated hot-dip galvanized steel sheet, which is suitable for use at the part of heating due to low film discoloration or damage caused by the heat. Eco Frontier™ JM shows high corrosion resistances after heating and bend section as well as a flat panel, because the inorganic layer has stronger adhesion capability by forming reaction products at the interface with a zinc coating layer. It also produces an excellent barrier effect by metal oxide to form an inorganic polymer and a self-healing effect by novel corrosion inhibitor. JM can be applied in various parts as an alternative to conventional chromate coated steel sheet.

1. Introduction

In response to global concern regarding environmental harmony in recent years, heightened efforts have been made to reduce environmental load substances, as seen in "Green Procurement" initiative and similar programs. Similarly, in coated steel sheets, this has led to a changeover from conventional chromate-treated steel sheets to chromate-free steel sheets which do not contain hexavalent chromium[1)]. In anticipation of these environmental needs, JFE Steel previously developed a series of high performance chemical conversion-treated steel sheets, "Eco Frontier™," which provides a combination of properties such as electrical conductivity, corrosion resistance, anti-fingerprint property, sliding property, etc.[2,3)].

Table 1 shows the JFE Steel lineup of chromate-free chemical conversion-treated steel sheets based on hot-dip galvanized (GI), hot-dip galvannealed (GA), and galvalume (GL) steel sheets. Products based on hot-dip galvanized sheets offer advantages in comparison with electrogalvanized products, in that sacrificial corrosion protection is superior, as heavy Zn coating weights can be realized with comparative ease, and higher corrosion resistance is achieved in galvalume sheets by adopting a 55%Al-Zn coating composition. For this reason, hot-dip galvanized materials are widely used in products and parts for severe corrosion environments, including major appliances such as refrigerators and washing machines, and in outdoor applications such as the outdoor units of air-conditioners, vending machines, water heaters, etc.

As a new line in the Eco Frontier™ series, JFE Steel recently developed a chromate-free coated GI, "Eco Frontier™ JM" (hereinafter, JM), with an inorganic coating film, which is suitable for use in parts that are

Table 1 "Eco Frontier™" Series on hot-dip galvanized steel sheet

Base metal	Classification	Designation	Characteristics
Pure Zn (GI)	General Use	JC	Organic coat
		JM	Inorganic coat
Zn-Fe (GA)	General Use	JC	Organic coat
55%Al-Zn (GL)	High corrosion resistance	JK	Anti-scratching
	High lubricity	JW	Excellent corrosion resistance

GI: Hot-dip galvanized steel sheet
GA: Hot-dip galvannealed steel sheet GL: Galvalume steel sheet

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subjected to heating in the manufacturing process[4–7]. This paper describes the features of this new product.

2. Development Concept

2.1 Discoloration and Damage of Coating by Heating

Organic resin components are included in the coating films of many chromate-free chemical conversion-treated steel sheets. In particular, a coating layer consisting mainly of organic components is used in many products for applications in which corrosion resistance is a priority, as a thick coating can be formed relatively easily[8]. However, when chemical conversion-treated steel sheets of this type are applied to parts that are subjected to high temperature heating in the manufacturing process, the heating process may cause discoloration and poor external appearance. This is attributed mainly to pyrolysis of the organic components and is a phenomenon that was not observed in chromate-type chemical conversion-treated steel sheets, in which the coating composition is mainly inorganic. As an example of products in which heat discoloration must be considered, the heat exchanger units of outdoor air-conditioners, etc. may be mentioned. In the process of brazing coolant circulation tubes to the steel sheets, the steel sheet in the vicinity of the brazed part is heated and exposed to high temperature.

Photo 1 shows the appearance of a conventional steel sheet with a chromate-free coating layer consisting mainly of organic resin components (hereinafter, conventional organic chromate-free material). The photo also shows the appearance of the same material when heated to a sheet temperature of 500°C in an infrared heating furnace, held at that temperature for 30 s, and then air-cooled to room temperature to simulate the above-mentioned heat-damaged part. The chromate-free coating was discolored to a reddish-brown color by heating, and also displays a cracked appearance. **Figure 1** shows the results of electron probe microanalyser (EPMA) mapping analysis of the coating before and after heating. Overall, the decrease in the intensity of C and increase in the intensity of Fe is remarkable, and the decrease in the intensity of C in the cracked area is particularly pronounced. **Photo 2** shows the results of scanning electron microscope (SEM) observation of the portion that was discolored after heating from a diagonal direction. As the chromate-free resin coating could not be observed in the cracked area, it can be understood that only the underlying Zn coating of the steel sheet remained in fragments after heating. Moreover, when the cracked area was observed, roughness had occurred at the surface of the Zn coating of the base material.

Based on these results, it is considered that heating caused alloying of the Zn of the Zn coating layer and Fe of the substrate steel sheet, thereby forming a Zn-Fe alloy. Since the chromate-free coating could not adequately follow the shape changes and volumetric expansion of that base, this resulted in separation and delamination of the chromate-free coating (**Fig. 2**). It is also thought that the appearance shown in Photo 1 resulted from pyrolysis and discoloration of the resin component caused by heating.

Photo 1 Appearance of conventional chromate-free coating before and after heating

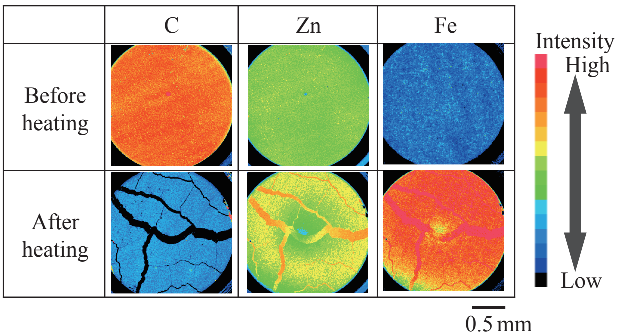

Fig. 1 Electron probe microanalyser (EPMA) analysis of surface of conventional chromate-free coating before and after heating

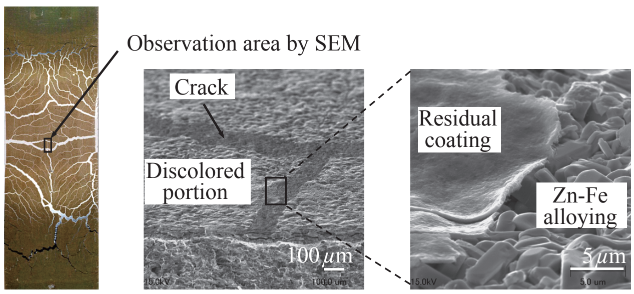

Photo 2 Scanning electron microscope (SEM) images of surface of conventional chromate-free coating after heating

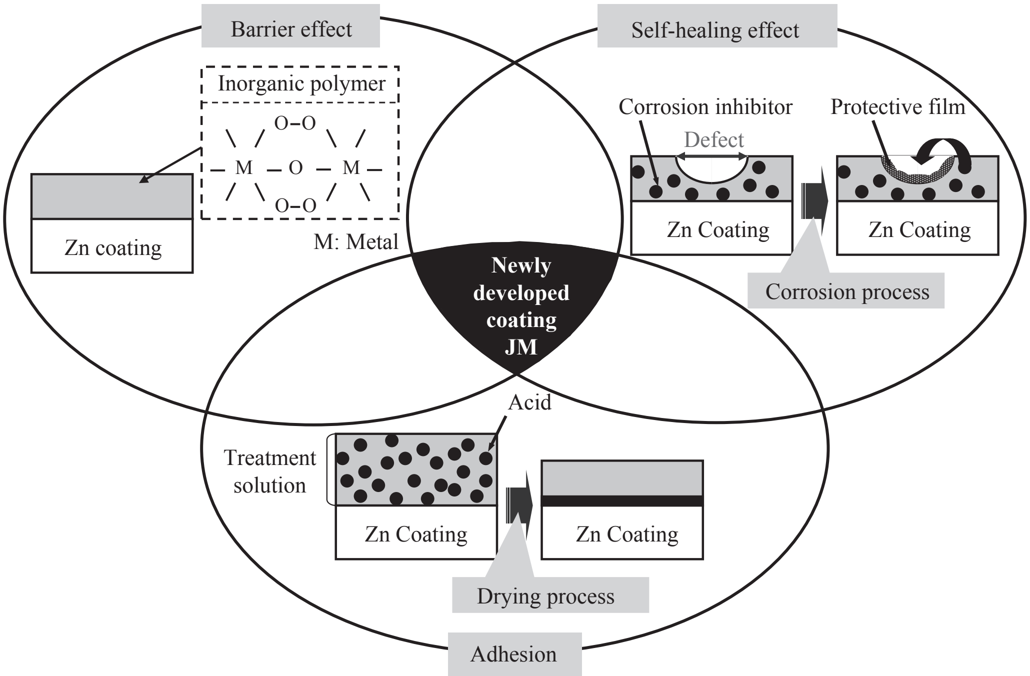

Fig. 3 Design concept of newly developed product: Eco Frontier™ JM

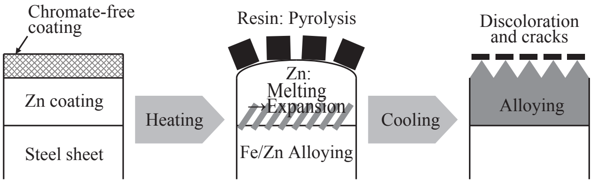

Fig. 2 Mechanism of discoloration and cracks on conventional chromate-free coating by heating

2.2 Concept of Coating Design

As shown above, if organic-based chromate-free materials are applied, there is a possibility of large changes in external appearance caused by heating in the part manufacturing process. Although this does not always become a problem, depending on differences in heating conditions, it may nevertheless become an obstacle to the changeover from conventional chromate-treated materials.

Minimizing the organic resin composition of the coating is effective for suppressing heat discoloration. Furthermore, even assuming stress is generated in the chromate-free coating during volumetric expansion of the Zn layer during heating, it is possible to alleviate this stress by micro coating damage, and thereby avoid large changes in external appearance, if the coating thickness can be reduced. However, a thin coating with high corrosion resistance is important, as reducing the thickness of the coating also reduces corrosion resistance.

Therefore, in order to reduce the organic resin composition and maintain high corrosion resistance with a thin film, a new product was developed on the basis of the know-how cultivated in the development of chromate-free chemical conversion-treated steel sheets to date, based on the following three concepts:

(1) Use of an inorganic polymer with a high barrier effect
(2) Self-healing effect by a novel corrosion inhibitor[9)]
(3) Strengthening of interfacial adhesion of reaction products by introducing an acid component in the treatment solution to etch the hot-dip Zn coating[10)]

As a result, a coating consisting mainly of inorganic components, which is suitable for use with a hot-dip galvanized base, was developed by utilizing a new metal oxide that forms an inorganic polymer. **Figure 3** shows the concept of the coating design.

3. Evaluation Method

3.1 Test Materials

The newly-developed inorganic chromate-free coating, JM (coating weight: 0.5 g/m^2) was applied to a GI (Zn coating weight: 40 g/m^2). The condition adopted in drying the coating was a maximum achieved temperature of 100°C using an induction heater. The comparison materials were chemical conversion-treated steel sheets

Table 2 Test Specimens

Key	Specimens (Coating weight)
Eco Frontier™ JM	Inorganic chromate-Free coating (0.5 g/m^2)
Sample A	Conventional chromate-Free coating containing approx. 90 mass% organic resins (1.0 g/m^2)
Sample B	Reacted-in-place chromate coating (20 mg/m^2 as Cr)

in which an organic chromate-free film (resin ratio: approx. 90%, coating weight: 1.0 g/m^2) or a chromate coating (Cr coating weight: 20 mg/m^2) was formed on the same steel sheet (**Table 2**).

3.2 Evaluation Method

3.2.1 Heat discoloration resistance

The samples were observed after heating to 500°C in the atmosphere in an infrared heating furnace, holding at that temperature for 30 s, and cooling to room temperature.

3.2.2 Corrosion resistance of flat area and bent section

The samples used in the corrosion test were flat sheets with the edges sealed, and bent sections in which 180° bending was performed with an inner radius of 2.5 mm. A salt spray test (SST; in accordance with JIS Z 2371 (JIS: Japanese Industrial Standard)) was performed, and the condition of white rust occurrence was observed.

3.2.3 Corrosion resistance of flat area after heating

After heating the flat panels as described in section 3.2.1, the edges were sealed, the SST test was performed, and the appearance of the samples was observed.

3.2.4 Spot weldability

Spot weldability was evaluated by the nugget diameter of specimens with a sheet thickness of 0.8 mm after a continuous spot welding test under the following conditions.

Electrode: Cr-Cu alloy DR (dome radius) type,
tip diameter: 6 mm
Electrode force: 2 000 N
Squeeze time: 30 cycles/50 Hz
Weld time: 10 cycles/50 Hz
Keep time: 10 cycles/50 Hz

4. Quality Properties

4.1 Corrosion Resistance of Flat Area

Photo 3 shows the corrosion resistance of the flat areas of the hot-dip galvanized based chromate-free chemical conversion-treated steel sheet JM developed in this work, which has a chromate-free coating consisting mainly of inorganic components, and sample A with a conventional organic resin coating and the chromate-treated material, sample B, which were used for comparison. "Eco Frontier^{TM} JM" showed only a minimal amount of white rust after 120 h of the salt spray test, and thus displayed excellent corrosion resistance, equal to that of samples A and B.

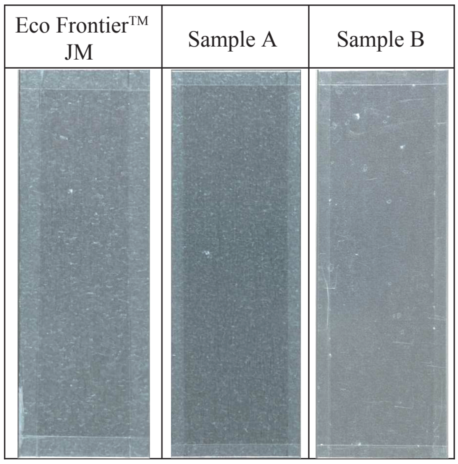

Photo 3 Appearance after 120 h of salt spray test (JIS Z 2371)

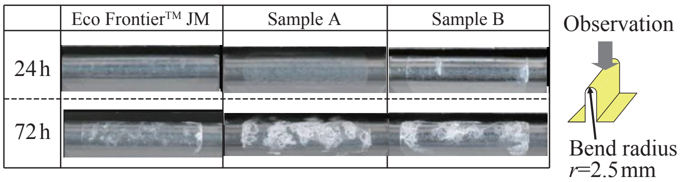

Fig. 4 Appearance of 180°bent section after salt spray test (JIS Z 2371)

4.2 Corrosion Resistance of Bent Section

Figure 4 shows the appearance of the 180° bent sections after 24 h and 72 h of the salt spray test. After 72 h, white rust was observed on the bent parts of samples A and B. In contrast, with JM, white rust generation was slight, and the developed material also displayed satisfactory corrosion resistance in the bending-forming part. This is attributed to the self-healing action of the novel corrosion inhibitor which is a component of the JM coating.

4.3 Resistance to Heat Discoloration

Photo 4 shows the appearance after heating. Sample A was discolored to a reddish-brown color, and formation of cracks was remarkable. In contrast, discoloration and cracking of JM were light, and the appearance of the JM sample was close to that sample B.

4.4 Corrosion Resistance of Heated Parts

Photo 5 shows the appearance of the heated samples after 24 h of the salt spray test. The condition of white rust on JM was similar to that of sample B, indicating corrosion resistance after heating on the same order as Sample B.

4.5 Spot Weldability

Figure 5 shows the transition of nugget diameter

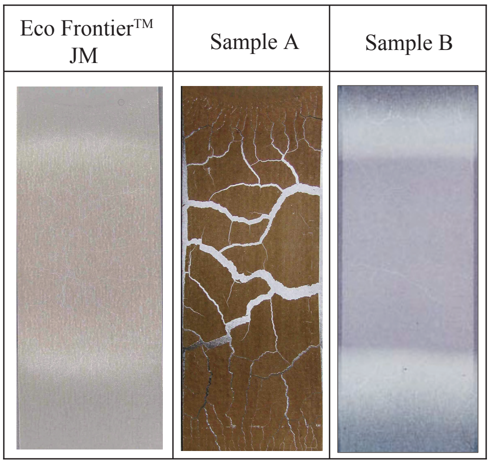

Photo 4 Appearance after heating

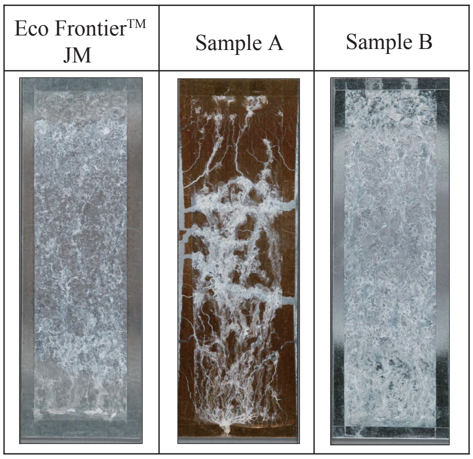

Photo 5 Appearance of heated specimens after 24 h of salt spray test (JIS Z 2371)

during continuous spot welding. With samples A and B, nuggets were no longer formed after approximately 400 spots, but in contrast, a stable nugget diameter was maintained with JM until 600 spots. This shows that JM also has excellent conductivity during welding due to its thin coating.

5. Conclusion

The concept and quality properties of the chromate-free coating design of “Eco Frontier™ JM,” which was developed in this research, were described in comparison with those of a conventional organic chromate-free steel sheet and chromate-treated steel sheet.

Because an inorganic chromate-free coating is used, JM displays minimal changes in appearance as a result of heating. As the JM coating also has high barrier effect and interfacial adhesion, as well as a self-healing function, it provides excellent corrosion resistance not only in flat panels, but also in bent and press-formed parts, and can be applied to parts and areas in which higher corrosion resistance is required under severe corrosion environments. Based on these properties, an expanded range of applications is expected.

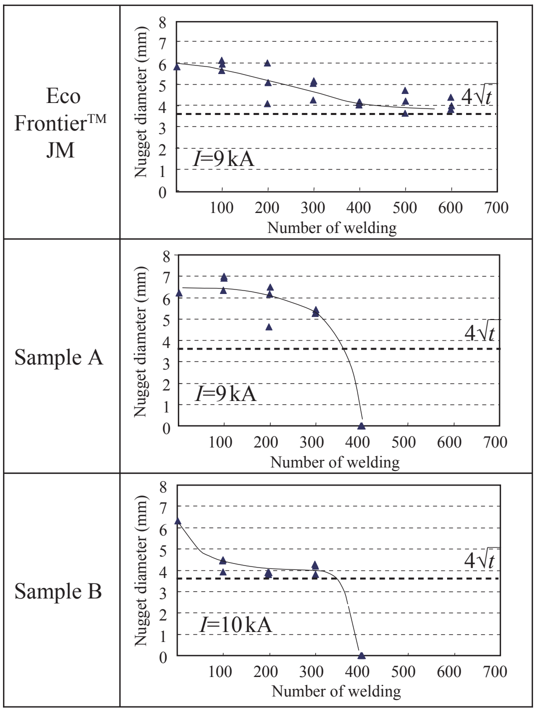

Fig. 5 Spot weldability

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