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Development of Chromate-Free Zn-5% Al-Based Alloy Coated Steel Sheet "ECOGAL-Neo™" EN

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Abstract:

A hot-dip Zn-5%Al steel sheet, ECOGAL™, has a surface appearance free from spangles by adding small amount of elements in plating and also has excellent corrosion resistance and blackening resistance. The chromate free coating on ECOGAL has properties of temporary rust prevention and good paint adhesion. However, when it is exposed to high temperature such as welding, discoloration of coating layer on ECOGAL may cause poor appearance. A new special chromate-free coated "ECOGAL-Neo™" EN was developed, and it is suitable for use at the part where heating is applied due to low film discoloration or damage caused by the heat. It also has properties of temporary rust prevention, good blackening resistance, formability and paint adhesion due to the treatment, which meet ecological requirements for building materials, electronic appliances, etc.

1. Introduction

Galvanized steel sheets are widely used in the electrical appliance, building material and automotive fields, etc., as zinc (Zn) displays excellent corrosion resistance in atmospheric environments and corrosion of the steel sheet is also suppressed by the sacrificial corrosion protection property of Zn[1]. Because durability and long life under outdoor environments are required in building materials, Zn-5% Al hot-dip galvanized steel sheets (GF: Galfan) with higher corrosion resistance, in which Al is added to the Zn plating layer, have been widely used until now[2]. However, in many cases, the appearance of this product was unsuitable, as it displays a nonuniform spangle pattern. On the other hand, ECOGAL™ has a uniform spangle-free appearance which is realized by adding a small amount of elements to the Zn-5% Al alloy coating, and it is also possible to maintain outstanding corrosion resistance equal or superior to that of the conventional Zn-5% Al hot-dip galvanized steel sheets[3].

As a chemical conversion treatment after coating, chromate treatment had long been used for temporary rust protection of the plating. In recent years, however, there has been a heightened necessity of conversion treatments that do not contain the environmental pollutant hexavalent chromium (Cr(VI)), and as a result, chromate-free technologies are now used[4]. Up to the present, various organic-inorganic composite coatings have been designed as substitute compositions with the white rust prevention function of chromate[5], but because chemical conversion-treated hot-dip galvanized steel sheets are processed into final products by forming, assembly, painting, etc., they must provide various types of performance, including not only white rust protection, but also resistance to discoloration (blackening) under high temperature, high humidity environments during transportation, as well as formability and paint adhesion. In addition, since spot welding, arc welding, etc. are performed to join steel sheets, these materials must also provide weldability and surface appearance after welding like that of the GI and GA hot-dip galvanized steel sheets which have been widely used for many years[6].

JFE Steel developed a chromate-free chemical conversion-treated Zn-5% Al-based alloy coated steel sheet "ECOGAL-Neo™" with a variety of outstanding properties, including white rust resistance, and began

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sales in December 2016. This report focuses on the quality properties of the chromate-free coating of ECOGAL-Neo.

2. Issues of Existing Chromate–Free Technologies

2.1 Coating Damage during Arc Welding

Product development of ECOGAL, which is a high corrosion resistance galvanized steel sheet, was completed in 2008, and this material has been widely used in building structural members such as columns and beams, building materials such as roofing and walls, steel flooring materials including grating and scaffold plates, frames for solar power generation system and in the agricultural and livestock fields, etc. Moreover, the outstanding properties of ECOGAL are not limited to corrosion resistance, but also include excellent formability, alkali resistance and weldability, and excellent temporary rust protection (white rust resistance) and paint adhesion can also be realized by forming a chromate-free coating on the surface of ECOGAL. However, when the chromate-free chemical conversion coating is heated to a high temperature with the steel sheet during welding, etc., discoloration or other appearance defects sometimes occur in the surrounding area due to heating. Since this phenomenon was rarely observed with conventional chromate coatings, it is recognized as a new issue. **Figure 1** shows the surface appearance around a weld after arc welding of sheets having a chromate-free chemical conversion coating with an organic-inorganic composite composition on an ECOGAL substrate (hereinafter, ECOGAL chemical conversion-treated steel sheet). Looking at the heat affected zone (HAZ) caused by welding, the sample displays a yellowish surface appearance due to discoloration of the chromate-free coating by heating, and cracks have also occurred. Therefore, the conditions for the occurrence of discoloration and cracks similar to that caused by welding were studied in the laboratory, and the cause was investigated.

ECOGAL
with conventional coating

Fig. 1 Surface appearances of ECOGAL with conventional coating after arc welding

2.2 Laboratory Simulation of Coating Damage Phenomena

2.2.1 Experimental method

An ECOGAL chemical conversion-treated steel sheet with a sheet thickness of 0.8 mm, which was produced on a hot-dip galvanizing line, was heated in an atmospheric air atmosphere so that the temperature reached 200 to 500˚C in 5 min, and after 5 min, the sheets were then removed from the heating furnace and slowly cooled in air to room temperature. The steel sheet surface after heating was evaluated from the two viewpoints of "cracking" and "yellow discoloration."

Next, in-situ observation was performed under the heating conditions that realized the above-mentioned coating damage. An environmental scanning electron microscope (environmental SEM: FEI, Quanta200FEG) was used, and observation was performed at an accelerating voltage of 10 kV under a 100 Pa O_2 atmosphere and results were recorded in every 5 seconds.

The changes in the states of components contained in the coating before and after heating were also investigated by X-ray photoelectron spectroscopy (XPS: Kratos, Axis Ultra DLD). In these measurements, a monochromatized AlK α beam (15 kV, 10 mA) was used as the X-ray source.

2.2.2 Results and discussion

Figure 2 shows the appearance of the ECOGAL chemical conversion-treated steel sheets after heating so as to reach the respective end-point temperatures in 5 min. Up to 300˚C, virtually no cracks or yellow discoloration were observed in the surface appearance, but discoloration occurred at 400˚C. When the final temperature was increased further to 500˚C, the width of the cracks increased, and a cracking pattern appeared over the entire surface of the steel sheet. It

300℃	400℃	500℃

Fig. 2 Surface appearances of conventional coating on ECOGAL after heating at the different temperature

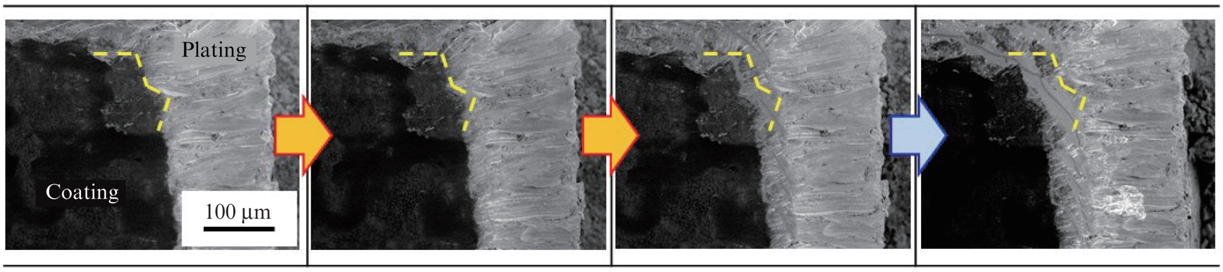

Fig. 3 Change of the surface appearance of coating during heating up to 500˚C

can be understood that this is similar to the surface appearance after welding. Based on these facts, it was found that discoloration and cracking can be simulated by heating to 500˚C.

Next, in order to clarity the mechanism responsible for the cracking, the ECOGAL chemical conversion-treated steel sheet was heated to around 500˚C, and that process was observed in-situ in real time using the environmental SEM. **Figure 3** shows secondary electron images of the sample corner part during heating. The region with the dark contrast is the chemical conversion coating, and the light region is the part of the steel sheet that was exposed by chamfering the sample edge. The edge of the chemical conversion coating before heating is shown by the broken line. As the temperature rises, the coating shrinks toward the sample center. From this, it is thought that cracks are caused by this kind of shrinkage of the coating. In addition, the fact that coating shrinkage occurs when the substrate plating (Zn-Al coating) melts was clarified for the first time by real-time observation.

Because coating shrinkage shows a relationship with melting of the plating, the same chromate-free coating as that on the ECOGAL chemical conversion-treated steel sheet was also formed on a cold-rolled steel sheet (hereinafter, CRS, melting point: approximately 1 500˚C), which has a melting point more than 500˚C higher than that of of ECOGAL (melting point: approximately 370˚C), and on a Zn-55% Al hot-dip galvanized steel sheet (Galvalume steel sheet: hereinafter GL, melting point: approximately 570˚C), and the influence of melting of the substrate was examined. **Figure 4** shows the surface appearance of these steel sheets after heating to 500˚C in the heating furnace. From these photographs, the cracks that were seen with the ECOGAL substrate were not observed with the CRS and GL substrates. Thus, these results demonstrated that the cracks after heating observed with ECOGAL occur due to melting of the plating by heating.

Focusing on Si, which is one component of the coating, **Fig. 5** shows the Si2p narrow spectra obtained by XPS measurements of the chemical conversion coated steel sheets before and after heating to 500˚C. A peak was observed at 102.5 eV in the coating before heating, but in contrast, the peak had shifted to 103.6 eV in the coating after heating to 500˚C. From this, it was understood that the structure of the Si composition changes when the material is heated to an elevated temperature.

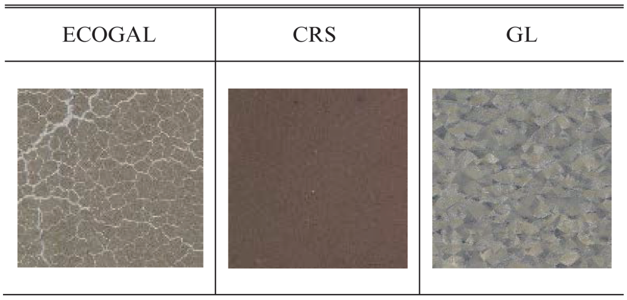

Fig. 4 Surface appearances after heating conventional coating on metals with different melting point

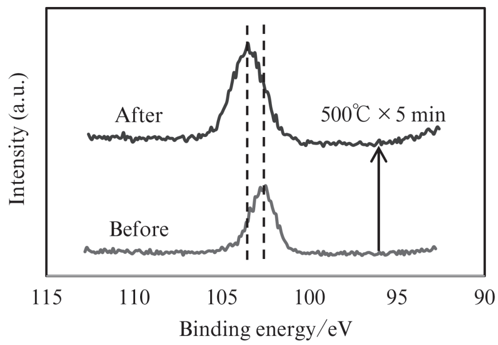

Fig. 5 Si2p spectra of the coating on ECOGAL before and after heating

Based on the results described above, it is thought that the cracks in the coating during heating occur by the process shown in **Fig. 6**. The chemical conversion coating shrinks due to heating, but if the coating is constrained by the plating of the substrate, shrinkage does not occur and internal stress accumulates in the coating. Although cracks do not occur in this stage, the plating melts when the temperature rises further and exceeds the melting point of the plating. When melting occurs, the chemical conversion coating is freed from

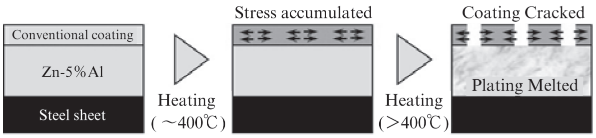

Fig. 6 Mechanism of cracks on conventional coating produced by heating

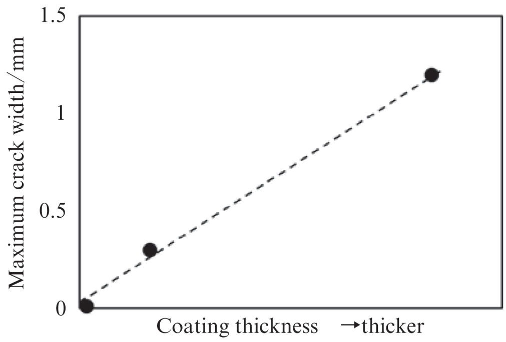

Fig. 7 The relation between maximum crack width and coating thickness

the constraint of the plating, and cracks occur in the coating due to the accumulated internal stress. Moreover, it is estimated that shrinkage of the coating, which causes the accumulation of internal stress, is triggered mainly by a structural change in the Si component contained in the chemical conversion coating.

The influence of the thickness of the chemical conversion coating of the ECOGAL chemical conversion-treated steel sheet on cracks was also investigated. **Figure 7** shows the results of an evaluation of the cracks that occurred after heating to 500˚C in the heating furnace. Here, cracking was evaluated by the maximum crack width. These results show the influence of the thickness of the chemical conversion coating on cracks. It can be confirmed that the crack width increases as the coating becomes thicker.

2.2.3 Concept of Coating Design to Prevent Coating Damage

As shown above, in order to prevent cracks during heating, reducing components that easily shrink due to structural changes during heating and applying components that are not susceptible to such structural changes are considered effective. Moreover, even if cracks occur due to the accumulation of internal stress in the coating, improvement is possible by relaxing that stress by microscopic coating damage and using a thinner coating that does not cause large changes in surface appearance. However, because reducing the contents of components that have a rust protection effect and using a thinner coating also reduce corrosion resistance, it is necessary to secure high corrosion resistance with a thinner film. Moreover, in addition to this requirement, blackening resistance, formability, paint adhesion and other desirable properties are also required. Therefore, an ECOGAL-Neo high performance chemical conversion coating with an excellent balance of these various performance properties (ECOGAL-Neo EN) was also developed by (1) using components which display little structural change due to heating, (2) making an organic-inorganic composite coating denser and its barrier property higher and (3) applying a high lubricity wax considering the softening point.

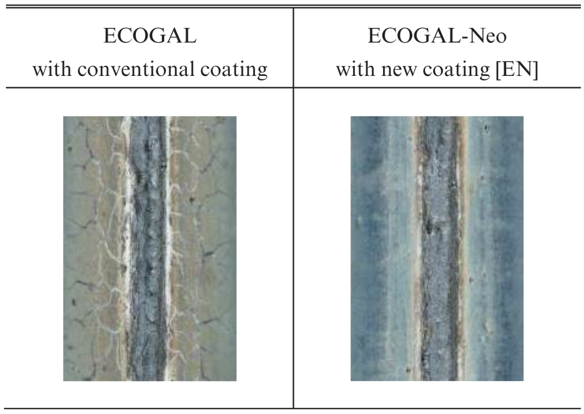

Fig. 8 Surface appearances after arc welding

3. Features of Developed Chromate–Free Coating

3.1 Coating Appearance after Heating by Simulating a Weld

Figure 8 shows the surface appearance of a Zn-5% Al hot-dip galvanized steel sheet ECOGAL-Neo (coating weight: 70 g/m^2) with the newly-developed chromate-free coating EN. In contrast to the remarkable discoloration and cracks which occurred with the conventional ECOGAL chemical conversion coated steel sheet, no large changes in surface appearance could be seen in the HAZ of the sheet with the developed EN coating, and discoloration and cracking of the coating did not occur even under heating to 500˚C.

3.2 Other Quality Properties

3.2.1 Corrosion Resistance of Flat Sheet

A salt spray test (SST, JIS Z 2371) of a flat portion was performed by sealing the edges. The area ratio of white rust which occurred on the new ECOGAL-Neo EN and the conventional ECOGAL chemical conversion treated steel sheets is shown in **Fig. 9**. Only very slight white rust could be observed after a 240 h SST, indicating that white rust resistance is not reduced by improvement of surface appearance after heating, and the newly-developed product has satisfactory white rust

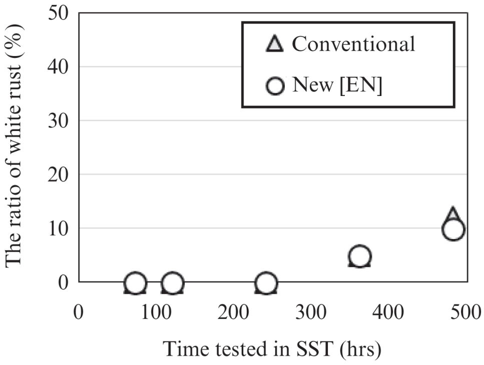

Fig. 9 White rust ratio of the coatings by SST

ECOGAL with conventional coating	ECOGAL-Neo with new coating [EN]
	

Fig. 10 Surface appearances after atmospheric corrosion test in Okinawa

resistance equal to that of the conventional ECOGAL chemical conversion treated steel sheet. **Figure 10** shows the appearance of the flat portions of samples after an atmospheric exposure test in a subtropical island environment in Okinawa for 1.5 years. In this exposure environment as well, remarkable white rust did not occur on ECOGAL-Neo EN, and the newly-developed product displayed satisfactory corrosion resistance. These results were similar to those with the conventional ECOGAL chemical conversion treated steel sheet.

3.2.2 Blackening resistance

Figure 11 shows the results of blackening resistance (change over time in lightness *L*) when ECOGAL-Neo EN and ECOGAL chemical conversion treated steel sheets were allowed to stand for 2 weeks in a temperature and humidity testing chamber controlled to an atmosphere with a temperature of 65°C and relative humidity of 98%. The *L* value of ECOGAL-Neo EN maintained a level of 60 or higher even after 2 weeks, thus showing higher blackening resistance than the ECOGAL chemical conversion treated steel sheet.

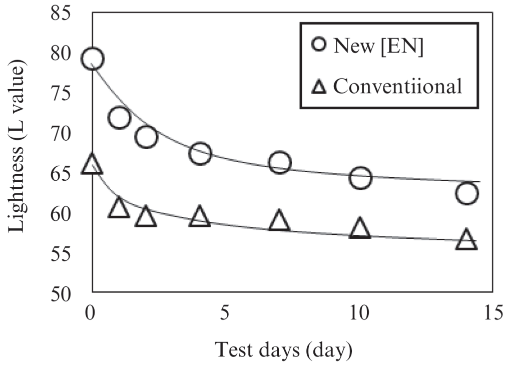

Fig. 11 Changes of L value on the coatings in high humid condition (65°C, 98%RH)

Table 1 The properties of ECOGAL-Neo EN

Properties	ECOGAL-Neo	ECOGAL
Appearances after heating	○	△
White rust resistance	○	○
Blackening resistance	◎	○
Friction coefficient	◎ (0.13)	○ (0.20)
Paint adhesion	○	○

3.2.3 Formability

As an index of formability, the friction coefficients calculated by sliding ECOGAL-Neo EN and ECOGAL chemical conversion treated steel sheets without a lubricant oil coating under conditions of a surface pressure of 130 MPa and sliding speed of 1.0 m/min are shown in **Table 1**. Under the unlubricated condition, the value of ECOGAL-Neo EN was lower than that of the ECOGAL chemical conversion treated steel sheet, showing that superior formability can be expected in press forming and other types of forming.

3.2.4 Paint adhesion

Table 1 also shows the results of a peeling test of a paint coating with adhesive tape by the following procedure. As a pretreatment, the samples were sprayed for 2 min with an alkaline degreasing agent at 60°C, then washed with water and dried. Next, a melamine alkyd resin paint was applied to the test pieces, which were then baked for at 130°C for 30 min to form a paint film with a thickness of 30 μm. The samples were immersed in boiling water for 2 h and immediately cut to the steel substrate in a lattice pattern. Cupping to a height of 5 mm was then performed with an Erichsen cupping machine, adhesive tape was fixed on the sample and peeled off, and the surface appearance after peeling was observed. As a result, both the ECOGAL-Neo EN and the ECOGAL chemical conversion treated steel sheet displayed satisfactory paint adhesion, with no peeling even in the part that was cut in the lattice pattern.

4. Conclusion

The design concept of the coating of the ECOGAL-Neo EN developed in this work and a comparison of the quality properties of the developed product with those of the conventional ECOGAL chemical conversion treated steel sheet were described. ECOGAL-Neo EN has satisfactory surface appearance after heating, and also has excellent temporary rust resistance (white rust resistance), blackening resistance, formability, paint adhesion and other properties. Based on this outstanding performance, use in a wide range of applications as a material for electrical appliance, building materials and the automotive field is possible, and expanded application is expected.

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