Zn-Fe/Zn-Ni Double-layer Electroplated Steel Sheet*

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Synopsis

A new double-layer electroplated steel sheet has been developed, which is composed of an upper Zn-Fe layer provides good paint adhesion and a lower Zn-Ni layer intended to improve corrosion resistance. Nickel content of 10~15 % and iron content more than 80 % were desirable.

Besides corrosion resistance, the steel sheet exceeded the conventional coated steel sheets also in the properties such as paint adhesion, workability and spot weldability.

I. Introduction

Corrosion of autobody can be broadly classified into two categories; corrosion from inside which occurs at the inner side of the parts such as door and sill, and the corrosion from outside which occurs at the exterior surfaces of the parts such as fender, hood and door.

Corrosion from inside causes perforation and corrosion from outside brings about scab and filiform corrosion.

Therefore, coated steel sheet for autobody should have high resistance to these two kinds of corrosion. Besides them, good press formability and good spot weldability are also required.

In order to obtain high perforation corrosion resistance thick coated layer with strong galvanic action is preferable. From the view point of press formability and spot weldability, however, light coating is required. For the corrosion resistance of the painted steel sheet, paint adhesion is considered to play an important role. Therefore, coated steel sheet for autobody should have good paint adhesion and also high resistance to the occurrence of paint defects such as cratering during cathodic electropainting.

To meet such demands contradict each other, many kinds of zinc alloy plating with moderate galvanic corrosiveness have been developed.¹⁻⁵⁾ Among them, Zn-Ni electroplating is considered to be most applicable to the commercial production because of its high current efficiency and small range of fluctuation in Ni content. Unfortunately, however, adhesion of this alloy plated steel sheet to the electropaint film is not sufficient. According to the previous results, zinc phosphate of paint base suitable to obtain good paint adhesion and high scab corrosion resistance is Phosphophyllite,⁶⁾ which includes iron as its structural element. Iron ions in Phosphophyllite can not be supplied from phosphatizing bath but supplied from the surface of the substrate.⁷⁾ Hence, coating material with high iron content, such as Zn-Fe, is con-

sidered to be desirable to obtain good paint adhesion and high scab corrosion resistance.

As it is difficult for single plated layer to realize both good perforation and scab corrosion resistance, double-layer electroplated steel sheet which has a thin Zn-Fe layer over a thick Zn-Ni layer has been developed.⁹⁾ In this paper, fundamental aspects and characteristics of this steel sheet are described.

II. Testing Procedure

1. Materials

Materials used in this study are listed in Table 1.

2. Electroplating

Both Zn-Ni and Zn-Fe electroplating were carried out using sulfate bath.

The electroplated specimens prepared by the electrogalvanizing test plant were used for the investigation of workability, corrosion resistance after working and spot weldability. The electroplated specimens prepared in laboratory were used for all the other studies.

3. Painting

The following 3-coat paint system was applied.

- 1) Zinc phosphate treatment (dipping type)
"Granodine SD 2000" (Nippon Paint Co., Ltd)
- 2) Cathodic electropaint primer coating
- 3) Surfacer coating
- 4) Water sanding
- 5) Top coating

The process is the same as that commonly applied to automobile bodies in Japan. Paint film thickness of primer, surfacer, and top coat were 20 μm , 40 μm and 35 μm , respectively. Thickness reduction by water sanding was about 5 μm .

4. Proportion of Phosphophyllite

The proportion of phosphophyllite in the phosphate layer was analysed by the X-ray diffraction method⁶⁾ and was calculated by the following formula.

$$\text{Proportion of Phosphophyllite} = P/(P+H)$$

where, P : X-ray intensity diffracted from (100) plane of Phosphophyllite ($\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$)

H : X-ray intensity diffracted from (020) plane of Hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$).

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Table 1. Materials.

Symbols	Description	Coating weight (g/m ²)	Content of alloy elements
Zn-Fe/Zn-Ni	Zn-Fe/Zn-Ni double-layer electroplated steel sheet	Zn-Fe: 4 Zn-Ni: 16	Fe: 85 % Ni: 11 %
Zn-Ni	Zn-Ni alloy electroplated steel sheet	20	Ni: 11 %
CG-A	Galvannealed steel sheet	45	Fe: 13 %
EG	Electrogalvanized steel sheet	40	—
CR	Cold-rolled steel sheet	—	—

5. Wet Adhesion of Paint Film

Specimens were coated by 3-coat paint system. 2 mm spacing crosshatch cut was made upon the painted surface after immersing in deionized water for 240 hr at 40 °C. Then cellophane tape was applied and removed quickly. Specimens were ranked in five grades according to the proportion of paint loss.

Grade 1:	Proportion of paint loss	95~100 %
2:	„	60~ 95 %
3:	„	30~ 60 %
4:	„	5~ 30 %
5:	„	0~ 5 %

6. Corrosion Resistance

Corrosion resistance was first evaluated by the salt spray test. In the case of the specimens without painting, the period until red rust had formed on 1 % of the surface was measured.

In the case of the specimens with the electropainted film 20 μm thick, the width of blistering area from score was measured.

In order to determine perforation corrosion resistance, two kinds of cyclic corrosion test (CCT-1 and CCT-2) were conducted simulating the perforation corrosion of auto-body. CCT-1 was designed to simulate the corrosion near the mechanically damaged site of paint film. To the specimens for this test, the electropaint primer 20 μm thick was applied. Specimens were then scored. CCT-2 was conducted to simulate the corrosion of the hidden parts of the car body such as inner side of a door. On such a part, even an enough coating of electropaint primer can not be provided. Therefore, only 10 μm thick electropaint primer was applied to the specimens for this test and the specimens were not scored. Test cycles of CCT-1 and CCT-2 are listed in Table 2. After these cyclic corrosion tests, corrosion depth and corrosion weight loss were measured.

7. Workability of the Plated Layer

During press forming, the plated layer is damaged by the abrasion between dies and also by the deformation of the steel substrate. To determine this behaviour, draw bead simulation test was carried out. Schematic representation of the draw bead simulation test is illustrated in Fig. 1.

After 200 specimens were continuously drawn, all

Table 2. Methods of cyclic corrosion tests.

Symbols	Description	Test cycle
CCT-1	Dipping in 5 % NaCl solution (50 °C×3 hr)	24 hr/cycle
	↓	
	Drying at room temperature (2 hr)	
	↓	
CCT-2	Salt spray test (50 °C×16 hr)	24 hr/cycle
	↓	
	Drying (50 °C×3 hr)	
	↓	
	Salt spray test (50 °×9 hr)	
	↓	
	Drying (70 °C×2 hr)	
	↓	
	Dipping in 5 % NaCl solution (80 °C×1 hr, and then 60 °C×1 hr)	
	↓	
	Drying at room temperature (2 hr)	
	↓	
	Salt spray test (50 °C×2 hr)	
	↓	
	Drying (70 °C×2 hr)	
	↓	
	Dipping in 5 % NaCl solution (80 °C×1 hr, and then 60 °C×1 hr)	
	↓	
	Drying at room temperature (2 hr)

Fig. 1. Schematic representation of the draw bead simulation test.

specimens and dies were rinsed by tri-chloroethylene. Metal powder produced during working was collected by filtrating the tri-chloroethylene and then weighed.

The damage of the plated layer was evaluated by the amount of metal powder. Elongation of the specimen was changed by controlling hydraulic pressure.

8. Cathodic Electropaintability

Electropaintability of various kinds of coated steel sheet was studied. Painting condition was as follows;
 Temperature: 28~30 °C
 Electrode area ratio: 1/1
 Applied voltage: 150~350 V
 Paint: "Power Top U-30" (Nippon Paint Co., Ltd.)

Electropaintability was evaluated by the minimum voltage required to initiate cratering.

9. Spot Weldability

Spot welding conditions used in this study are as follows;

Spot welder: direct spot welder
 Electrode tip: 6 mm ϕ , Cr-Cu (RWMA class 2) dome type (Fig. 2)
 Electrode force: 200 kgf
 Squeeze time: 40 cycles
 Holding time: 20 cycles
 Welding time: 12 cycles

Optimum current range and the electrode life were measured. Before determining optimum current range, a series of 150 welds of cold-rolled steel sheet was spot welded to obtain a good electrode face condition. In this case, constant welding current of 10 kA was adopted.

III. Fundamental Aspects of Double Layer Electroplated Steel Sheets

1. Nickel Content of Lower Layer

Lower layer is a layer for guaranteeing corrosion resistance. Figure 3 shows the relationship between nickel content of Zn-Ni alloy and the corrosion resistance. With the increase in nickel content, the period until 1 % of red rust observed increased and reached a maximum at the nickel content of 10~15 %, and then decreased. The crystal structure of Zn-Ni of these composition range was γ phase. The observations obtained here correspond favourably with the previous results.¹⁾ From the corrosion resistance and the sense of economy, nickel content of 11 % was chosen in this study.

2. Iron Content and Coating Weight of Upper Layer

In order to improve paint adhesion and scab corrosion resistance of Zn-Ni alloy plated steel sheet, thin Zn-Fe alloy was electroplated over Zn-Ni layer. (Fig. 4)

As mentioned above, formation of Phosphophyllite by zinc phosphate treatment is shown to be a significant reason for good paint adhesion and high scab corrosion resistance. Effect of iron content of Zn-Fe alloy on the proportion of Phosphophyllite was studied. The results are shown in Fig. 5. Phosphophyllite was observed in the specimens with the iron content of approximately 30 % and larger. The

Fig. 2. Cross section of the electrode tip.

Fig. 3. Relationship between nickel content of Zn-Ni layer and corrosion resistance. (by salt spray test)

Fig. 4. Schematic representation of Zn-Fe/Zn-Ni double-layer electroplated steel sheet.

Fig. 5. Effect of iron content of Zn-Fe alloy on the proportion of Phosphophyllite.
 (Zn-Fe: 4 g/m², Zn-Ni (11 %): 16 g/m²)

proportion of Phosphophyllite increased with increasing iron content. Scanning electron micrographs of phosphate coatings are shown in Photo. 1. With the increase in iron content, almost rectangular crystals of Phosphophyllite began to be observed among narrow leaflike crystals of Hopeite. In the case of 82 %

Photo. 1. Scanning electron micrographs of phosphate coating on various Zn-Fe plated layers.

iron, leaflike crystals of Hopeite were no longer observed and almost the same crystals as those formed on cold-rolled steel sheet were observed.

Figure 6 shows the results of wet adhesion test on the specimens painted by 3-coat paint system. Wet adhesion was remarkably improved in the specimens with the iron content greater than approximately 30 %. Salt spray test results given in Fig. 7 on the electropainted specimens also show that high iron content causes high resistance to blistering.

From the results mentioned above, it is desirable that the iron content of upper Zn-Fe alloy layer is more than 80 %. In the case of 100 % Fe, good phosphate crystals could not be obtained and the width of blistering slightly increased.

Fig. 6. Effect of iron content of Zn-Fe alloy on the wet adhesion of paint film.
(Zn-Fe: 4 g/m², Zn-Ni (11 %): 16 g/m²)

Fig. 7. Salt spray test results of electropainted double-layer electroplated steel sheets.
(Zn-Fe: 4 g/m², Zn-Ni: 16 g/m², electropaint: 20 μm)

Because the main role of the upper layer is the improvement of paint adhesion, heavy coating is not necessary. Figure 8 shows the effect of coating weight of Zn-Fe layer on the blistering behavior of electropainted specimen.

In the coating weight range of the upper layer over 2 g/m², blistering was kept in a low level. Coating weight of this layer ought to be controlled taking the deterioration of the coating layer during press forming into account. In Fig. 8, test results of the specimens electropainted after the draw bead simulation test are also shown. Observations on worked specimens almost coincide with that on unworked specimens.

IV. Properties of Double-layer Electroplated Steel Sheet

Properties of Zn-Fe/Zn-Ni double-layer electroplated steel sheets (Zn-Fe/Zn-Ni) were investigated in comparison with the conventional electrogalvanized (EG), hot dip galvanized (CG-A), and Zn-Ni electroplated (Zn-Ni) steel sheets.

1. Paint Adhesion

Figure 9 shows the wet adhesion test results. Wet adhesion of Zn-Ni was in almost the same level as that of conventional EG and markedly inferior to that of cold-rolled steel sheet. Wet adhesion of Zn-Fe/Zn-Ni was as good as that of cold-rolled steel sheet.

2. Corrosion Resistance

Blistering behaviour in salt spray test was determined on the electropainted specimens. Results are shown in Fig. 10. Width of blistering area from score of Zn-Fe/Zn-Ni was the smallest of all and was in the same level as that of cold-rolled steel sheet. Cyclic corrosion test results are given in Figs. 11 to 13. Figure 11 is the results of CCT-1. Corrosion resistance of Zn-Fe/Zn-Ni was in almost the same level as that of Zn-Ni and slightly lower than that of CG-A and EG. For the corrosion of this kind, effect of coating weight of plated layer is considered to be significant. Although the data are not shown here, corrosion resistance of Zn-Fe/Zn-Ni with increased coating weight of 30 g/m² (Zn-Fe: 4 g/m², Zn-Ni: 26 g/m²) exceeds that of CG-A. Figures 12 and 13

Fig. 8. Effect of coating weight of the Zn-Fe layer on the width of blistering by the salt spray test.
(electropaint: 20 μm)

Fig. 9. Wet adhesion of paint film on various coated steel sheets.

Fig. 10. Blistering behaviour of various coated steel sheets.
(electropaint: 20 μm)

are the results of CCT-2. Corrosion resistance of Zn-Fe/Zn-Ni was excellent in both corrosion depth and blistering rate.

3. Workability of Plated Layer

Production of metal powder by the flaking off of deposited metal during press forming was determined by the draw bead simulation test. The results are

Fig. 11. Maximum corrosion depth after 30 cycles of cyclic corrosion test.
(CCT-1, electropaint: 20 μm)

Fig. 12. Corrosion depth after 35 cycles of cyclic corrosion test.
(CCT-2, electropaint: 10 μm)

Number: rating number based on blistered area
Vs~Vl: size of blister
vs: very small
s: small
m: medium
l: large
vl: very large

Fig. 13. Blistering behaviour in cyclic corrosion test.
(CCT-2, electropaint: 10 μm)

shown in Fig. 14. In the case of CG-A, the amount of metal powder increased to a great extent with the increase in elongation. In the case of EG, however, only a small amount of powder was produced. The amount of powder from the specimens of Zn-Fe/Zn-Ni was even less than that of EG. As shown in Photo. 2, many cracks were observed on the surfaces

Fig. 14. Amount of powder produced by draw bead simulation test.

of Zn-Fe/Zn-Ni and CG-A, which was not the case with EG. Micrographs of the metal powder are shown in Photo. 3. From EG, large flakes came off. The size of particles of metal powder decreased, with EG giving off the largest particles, then Zn-Fe/Zn-Ni and CG-A giving off the smallest of particles.

Because the plated layers of Zn-Fe/Zn-Ni are harder than EG, large flakes of deposited metal do not come off easily. However, many cracks occur because the deformation rate of the hard plated layer is smaller than that of the steel substrate. In spite of the occurrence of small cracks, the production of metal powder during working of Zn-Fe/Zn-Ni is very small because of the excellent adhesion of plated layer to the steel substrate.

4. Corrosion Resistance after Working

The salt spray test was made of the specimens phosphated and electropainted after the draw bead simulation test. The results are shown in Fig. 15. Corrosion resistance of both kinds of steel evaluated by the width of the blistering area from the score is little influenced by the elongation in the draw bead simulation test. Zn-Fe/Zn-Ni has a much higher corrosion resistance than CG-A.

The proportion of Phosphophyllite in the phosphate crystals precipitated on the specimens phosphated after the draw bead simulation test is shown in Fig. 16. The phosphate crystals on unworked Zn-Fe/Zn-Ni are all Phosphophyllite. On the specimens after the draw bead simulation test, however, crystals of Hopeite also began to be observed, and the proportion of Phosphophyllite decreased with increasing elongation. In the case of CG-A, only Hopeite was observed in all specimens.

Micrographs of phosphate crystals on Zn-Fe/Zn-Ni are shown in Photo. 4. Zn-Ni layer was locally exposed at the crack produced by plastic working and Hopeite crystals seemed to grow preferentially at that place. Reduction of the proportion of Phosphophyllite by plastic working is considered to be explained by the above mentioned phenomenon. Good corrosion resistance of Zn-Fe/Zn-Ni shown in Fig. 15 could be attributed to the high proportion of Phos-

Photo. 2. Surfaces of various coated steel sheets after the draw bead simulation test. (SEM)

Photo. 3. Scanning electron micrographs of metal powder produced by draw bead simulation test.

Fig. 15. Corrosion resistance of specimens electropainted after draw bead simulation test. (electropaint, 20 μm)

Fig. 16. Influence of drawing on proportion of Phosphophyllite.

Photo. 4. Scanning electron macrographs of Zn-Fe/Zn-Ni phosphated after the draw bead simulation test.

phophyllite even on the deformed specimens.

5. Cathodic Electropaintability

Occurrence of crater during cathodic electropainting is one of the large problems in the painting process of auto-body. Crater is a kind of defect of paint film and the occurrence is largely affected by the applied voltage, the kind of steel sheet, and the properties of paint itself. In this study, minimum voltage to initiate cratering (V_c) was examined on various kinds of steel sheets. The results are given in Fig. 17. In the case of CG-A, V_c was very low. While, V_c on Zn-Fe/Zn-Ni was as high as 300 V. This is the same level as that on cold-rolled steel sheet.

6. Spot Weldability

Optimum current range for spot welding is shown in Fig. 18. Optimum current ranges on Zn-Fe/Zn-Ni and on cold-rolled steel sheet almost overlapped each other. This fact suggests that the same welding condition as cold-rolled steel sheet can be adopted for the welding of Zn-Fe/Zn-Ni. Figure 19 shows the results of spot weld electrode life test. Electrode life for Zn-Fe/Zn-Ni was about twice that for CG-A.

As mentioned above, spot weldability of Zn-Fe/Zn-Ni was markedly improved in comparison with conventional CG-A. This is considered to be due to the high melting temperature⁸⁾ of the deposited metal and small coating weight of Zn-Fe/Zn-Ni.

V. Conclusions

Double-layer electroplated steel sheet composed of an upper Zn-Fe layer and a lower Zn-Ni layer has been developed. Zn-Ni layer is intended to improve corrosion resistance and Zn-Fe layer provides good paint adhesion and the corrosion resistance after painting. According to the fundamental study, nickel content of 10~15 % and iron content more than 80 % were desirable.

Corrosion resistance, paintability, workability and spot weldability were investigated on the steel sheet with the coating weight of 20 g/m² comparing with conventional hot dip galvanized and electro-galvanized steel sheets. Results obtained are as follows:

(1) Wet adhesion and the resistance against blistering of double-layer electroplated steel sheet were the best of the group of materials.

Fig. 17. Relationship between painting voltage and occurrence of cratering.

Fig. 18. Optimum current range for spot welding.

Fig. 19. Results of spot weld electrode life test.

(2) The cyclic corrosion test (CCT-2) was conducted on the lightly electropainted and non-scored specimens simulating the corrosion of the hidden part of car body. Double-layer electroplated steel sheet showed the highest perforation resistance, despite of its small coating weight.

(3) Another cyclic corrosion test (CCT-1) was conducted on the electropainted and scored specimens

simulating the perforation at the mechanically damaged site of paint film. For the corrosion of this kind, coating weight of double-layer electroplated steel sheet as low as 20 g/m² was insufficient. Slightly increased coating weight is required.

(4) Double-layer electroplated steel sheet exceeded the other coated steel sheets also in the properties such as spot weldability, workability and the corrosion resistance after working.

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