Development of Ni-Zn Alloy Plated Steel Sheet*

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Synopsis

Nickel-zinc alloy electroplated steel sheet has been developed for automobile body protection as a pre-coated sheet which has a good corrosion resistance even with light coating weight.

The Ni-Zn alloy plated sheet with a gamma phase film shows the best corrosion resistance among Ni-Zn alloy films and has the excellent perforation resistance even without electrocoat in some types of cyclic corrosion test.

In addition, this product satisfies the fundamental properties required as a pre-coated steel sheet for automobiles, e.g., formability, weldability and paintability.

Therefore, this Ni-Zn alloy electroplated steel sheet is suitable for the enclosed portion of automobile body panels which is susceptible to perforation due to insufficient electrocoat.

I. Introduction

Recently, corrosion in automobile bodies has become a serious problem due to using of a lot of deicing salt. This corrosion type is mainly perforation which initiates on the enclosed side of insufficiently coated panels or joints in which water is easily trapped.¹⁾

To improve the corrosion resistance, electrogalvanized steel sheet has been requested because of its advantages;

(1) It is available for deep-drawn parts because the mechanical properties of substrate are hardly changed during electroplating.

(2) One side plated steel sheet can be easily produced.

(3) It is suitable for light coating.

(4) Coated films with various composition are attained by changing bath composition.

However, electrogalvanized steel sheet has to increase its coating weight to increase the corrosion resistance, which causes flake off in deformation and deterioration in weldability.

Therefore, several types of new electroplated steel sheet have been developed to improve the corrosion resistance of electrogalvanized steel sheet.²⁻¹⁴⁾

The electrodeposition of Ni-Zn alloy under low current density has been investigated¹⁵⁾ and its high corrosion resistance is well-known.¹⁶⁾ However, the deposition under high current density, the corrosion resistance and other properties as a coated steel sheet have not been evaluated yet.

The present investigation is concerned with the production, the corrosion behavior, and fundamental properties of Ni-Zn electroplated steel sheet.

II. Fundamental Investigation

1. Selection of Ni-Zn Alloy

Fundamental investigation was carried out with sulfate baths containing nickel, zinc, and sodium ions. The films of 4.8~37.3 % Ni content were deposited from the baths with various concentration ratio of nickel ion to zinc ion.

The corrosion resistance of the deposited film was estimated with the ASTM B-117 salt spray test. Photograph 1 shows the corroded appearance of Ni-Zn alloy of various nickel contents. Figure 1 shows the influence of a nickel content on the red rust occurrence. The grey film with a lustrous appearance of 10 to 16 % Ni content had the best corrosion resistance approximately eight times as much as that of electrogalvanized steel sheet.

The crystal structure was analyzed with an X-ray diffractometer. The best corrosion resistance was attained when a single phase of gamma (γ) was formed, while the mixed phase of eta and gamma ($\eta+\gamma$) was observed at a lower nickel content and gamma and alpha ($\gamma+\alpha$) at a higher nickel content.⁴⁾

2. Deposition of Ni-Zn Alloy

In a continuous plating on a strip, the adoption of higher current density is beneficial to reduce production cost. Figure 2 shows the relationship between nickel content of a deposited film and $\text{Ni}^{2+}/(\text{Zn}^{2+} + \text{Ni}^{2+})$ molar ratio of plating solution. The γ phase alloy was deposited preferentially from the wide range of $\text{Ni}^{2+}/(\text{Zn}^{2+} + \text{Ni}^{2+})$ molar ratio under either 5 A/dm² or 20 A/dm².

In actual production, movement of a strip and agitation of plating solution have an effect on film composition. To investigate the effect of the agitation, an additional plating test was performed in the plating cell in which the flow velocity of the plating solution was controlled. Figure 3 shows the influence of these plating conditions on the nickel content of the film when the molar ratio of nickel ion to zinc ion in the bath was three. The nickel content increased with increased current density. However, the preferential formation of the γ phase was assured when the velocity of more than 20 m/min was maintained.

The stable Ni-Zn alloy plating on a steel sheet under high current density has been clarified by keeping the sufficient flow velocity of the plating solution

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and the proper range of the molar ratio of nickel ion to zinc ion.

3. Production in Conventional Line

Trial production was done in the conventional elec-

troplating line based on the experimental results.

Table 1 shows the distribution of a nickel content of the trial coated coil. After specimens cut off from each coil were dissolved in hydrochloric acid, nickel and zinc concentrations were measured with atomic

Fig. 1. Effect of nickel content of deposited Ni-Zn alloy film on corrosion resistance (in salt spray test).

Fig. 3. Effect of current density and flow velocity on nickel content of deposited film (pH 2, 50 °C).

Fig. 2. Relation between nickel content of deposited film and $\text{Ni}^{2+}/(\text{Zn}^{2+} + \text{Ni}^{2+})$ molar ratio in bath.

Ni content (%)	Exposure time in salt spray test (day)								
	1	2	3	4	5	6	7	8	9
0									
4.8									
12.7									
29.0									

Photo. 1. Appearance of Ni-Zn alloy films (20 g/m²) after salt spray test.

SZ: Ni-Zn alloy plated steel sheet (20 g/m²)
GI: Hot-dip galvanized steel sheet (60 g/m²)
GA: Galvannealed steel sheet (40 g/m²)
CR: Cold-rolled steel sheet

Photo. 4. Appearance of 5 μm E-coated panels after 75 cycle exposure in the Cycle Corrosion Test II.

absorption analysis. The deposited film of 12.0 to 13.4 % Ni content consisting of the γ phase was obtained. This electroplated sheet also had a lustrous appearance where no dislocation of nickel was detected on the surface with EPMA as shown in Photo. 2.

4. Corrosion of Ni-Zn Plated Steel Sheet

The high corrosion resistance of Ni-Zn alloy plated steel sheet was confirmed by the electrochemical measurements in 5 % sodium chloride solution.

Figure 4 shows the influence of a nickel content on the corrosion current measured with polarized resistance method. The γ phase film of approximately 13 % Ni content shows the least corrosion current density. This film is considered to have the best corrosion resistance as well as showing the most delayed occurrence of red rust.

Figure 5 illustrates the effect of nickel content on corrosion potential. Though corrosion potential increases with increases in a nickel content, the potential of γ phase film was much less than that of iron. Thus, Ni-Zn steel sheet is expected to have the good protection.

5. Corrosion Behavior

Figure 6 shows the comparison of Ni-Zn alloy plated steel sheet (SZ) and electrogalvanized steel sheet (EG) in corrosion potential change. As corro-

sion proceeded, the potential of SZ shifted in the noble direction and close to the iron potential. This result means that the surface changes into less corrosive one and this change was supported by resulting weight loss during corrosion.

The corrosion products of Ni-Zn alloy plated steel sheet was found to consist of zinc compound including

Fig. 4. Effect of nickel content of deposited Ni-Zn alloy film on corrosion current density (i_c) in 5 % NaCl.

Fig. 5. Effect of nickel content of deposited Ni-Zn alloy film on corrosion potential in 5 % NaCl.

Table 1. Distribution of nickel content (%) of Ni-Zn alloy electroplated steel sheet.

Coil No.	Position				
	5 cm inside from edge	1/4 L*	1/2 L	3/4 L	5 cm inside from edge
A	12.0	12.4	12.6	12.4	12.6
B	12.3	12.3	12.4	12.6	13.3
C	12.7	12.3	12.4	12.6	12.6
D	13.0	13.3	13.4	12.6	12.7
E	12.6	12.9	13.2	13.3	12.6
F	13.0	13.0	13.0	13.2	13.1
G	13.4	13.2	13.3	13.0	13.0

* L: coil width

Photo. 2. Surface analysis of nickel and zinc in electroplated Ni-Zn alloy film with EPMA.

Fig. 6. Comparison of corrosion potential change of Ni-Zn alloy plated steel sheet (SZ) and electrogalvanized steel sheet (EG) determined in 5 % NaCl after salt spray exposure.

zinc hydroxide and zinc carbonate with X-ray photoelectron spectroscopy (XPS).

The nickel and zinc states of the corroded surface after removing corrosion product was also analyzed in depth with XPS. The results are shown in Figs. 7 and 8. On the dark grey surface, the enrichment of metal state nickel containing zinc corrosion product was observed. This means that the corroded surface will be covered with the nickel rich layer containing corrosion product due to the preferential dissolution of zinc of a Ni-Zn alloy film. Because of the passivity by this layer, Ni-Zn alloy plated steel sheet is considered to show much better corrosion resistance.

III. Properties of Ni-Zn Alloy Steel Sheet

Fundamental properties of Ni-Zn electroplated steel sheet suitable for an automobile body were investigated in comparison with the other types of commercial coated steel sheet:

- 1) Ni-Zn alloy electroplated steel sheet (SZ) (g/m²): 20, 30
- 2) Electrogalvanized steel sheet (EG) (g/m²): 20, 40, 60
- 3) Hot-dip galvanized steel sheet (GI) (g/m²): 60, 90
- 4) Galvannealed steel sheet (GA) (g/m²): 40, 45, 60
- 5) Cold-rolled steel sheet (CR)

1. Adhesion after Deformation

The adhesion of SZ film after deformation was estimated by the "Scotch Tape" peeling test. This result is shown in the strain diagram in which each type of deformation is classified by the combination of two principle strains, ϵ_x and ϵ_y . The comparison of SZ and GA in adhesion is shown in Fig. 9. SZ had favorable adhesion after all types of deformation. However, GA had severe flake off especially in deep drawing.

Another adhesion test was carried out. Figure 10 compared the flake off of SZ, EG, and GA in deep drawing. A 80 mm ϕ blank was deformed with drawing ratio of 2.0. The specimens were degreased and then weighed to evaluate the amount of flake off. SZ showed the least quantity, and thus SZ will be free from dent trouble in a stamping shop.

2. Weldability

Figure 11 shows the comparison of SZ and EG in nugget diameter change in consecutive spot welding to 5 000 points. One side plated 0.8 mm thick steel sheets were examined. SZ showed the similar spot weldability to EG with the same coating weight when each plated face was joined together, while the nugget diameter did not change significantly with increased coating weight when each uncoated face was joined together. However, in the case of SZ, the electrode surface is more smooth and less damaged in comparison with EG. This result possibly originates in the higher melting point and hardness of SZ film.¹⁷⁾

Because the coating weight of SZ is not so heavy

Fig. 7. State analysis of nickel on surface of Ni-Zn alloy plated film with XPS.

Fig. 8. State analysis of zinc on surface of Ni-Zn alloy plated film with XPS.

as EG to attain the same corrosion resistance, SZ will be more beneficial in spot welding.

3. Perforation

It is of common knowledge that the evaluation of perforation in salt spray test does not correspond with the field performance. Thus, some cyclic corrosion

Fig. 9. Adhesion strain diagram.

Fig. 10. Flake off of SZ, EG and GA in shrink flanging.

Fig. 11. Consecutive spot weldability.

Fig. 12. Comparison of perforation resistance on several products by Wet & Dry cycle test.

Fig. 13. Comparison of perforation resistance on several products by Cycle Corrosion Test I.

tests are recommended by auto manufacturers. The perforation of unpainted panels was investigated in the following cyclic corrosion tests:

Dry & Wet Cycle Test

Cycle Corrosion Test I¹⁸⁾

Cycle Corrosion Test II¹⁹⁾

The results were illustrated in Figs. 12 and 13, and Table 2, respectively. In each test, SZ showed the excellent perforation resistance.

4. Corrosion Resistance after Electrocoating

Phosphating is usually carried out before electro-

coating on automobile bodies. Figure 14 shows the comparison of the reactivity of SZ, EG, GA and CR in spray type phosphating (Nippon Parkerizing Co., Ltd. BT-137). SZ showed the high reaction rate in the initial stage of phosphating reaction but had the same weight of phosphate coating as CR in the final stage when the film was formed completely. This result originates in the rapid passivity of SZ surface in phosphating.

Photograph 3 shows the phosphated surface of various plated sheets. The phosphated film of SZ had the appearance in light grey as well as CR, and consisted of fine grains of Hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$).

Electrocoating was performed with a cathodic electrocoat. Cathodic electrocoating has brought a big improvement in the corrosion resistance if coated sufficiently. However, insufficiently electrocoated portions are inevitable in a mass production line, in which perforation initiates. Though such portions are post-coated with wax or sealer, the degree of protection achieved by the preventive measures is uncertain. Therefore the perforation resistance was evaluated with the insufficiently electrocoated panels.

Photograph 4 (see p. 924) shows the appearance of

Table 2. Perforation resistance of as-received pre-coated steels in Cycle Corrosion Test II.

Material	SZ 30 g/m ²	GI 90 g/m ²	GA 60 g/m ²	CR —
Maximum corrosion depth (mm) 30 days exposure	0.10	0.22	0.22	>0.79 (perforation)

Fig. 14. Growth of coating in zinc phosphating as a function of spraying time.

Photo. 3. Crystallography of phosphated film of several types of plated steel sheet analyzed with SEM.

a 5 μm cathodic electrocoated specimen without scribe after 75 cycle exposure in Cycle Corrosion Test II. The specimens were prepared in the following process:

Alkaline degreasing → Water rinsing →
(Ridoline #75*)
Surface conditioning → Zinc phosphating →
(Fixodine #5T0*) (Granodine #SD2000*)
Water rinsing → Chromic acid rinsing →
(Deoxylite #40*)
Water rinsing → Cathodic electrocoating
(Power Coat U-30*)

* from Nippon Paint Co., Ltd.

While CR has been covered with red rust yet, GI and GA showed many large blisters. However, SZ showed the excellent resistance against not only blistering but perforation.

IV. Summary

Ni-Zn alloy electroplated steel sheet (SZ) has been developed as a pre-coated steel sheet which has a good corrosion resistance even with light coating weight and maintain the mechanical property of the substrate.

The features of this product are summarized as follows:

- (1) SZ with a gamma phase film shows the best corrosion resistance among Ni-Zn alloy films.
- (2) The gamma phase film is deposited stably even under high current density by keeping the sufficient flow of plating solutions and the proper range of molar ratio of nickel ion to zinc ion in the bath.
- (3) SZ is produced in a conventional line and the product with a uniform composition is obtained.
- (4) Adhesion of SZ after deformation is much better than that of galvanized steel sheet.
- (5) Spot weldability of SZ is similar to that of electrogalvanized steel sheet with the same coating weight.
- (6) SZ has the excellent perforation resistance not only in an insufficiently electrocoated panel but also in an unpainted panel in some cyclic corrosion tests.

Therefore, SZ is suitable for the protection of automobile body panels, especially the enclosed portion which is susceptible to inside-out perforation because

of insufficient electrocoat.

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