Development of New Corrosion-resistant Steel Sheets for Automobiles*

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Synopsis
Three new types of corrosion-resistant steel sheets for automotive body panels have been developed.
1) Zinc–nickel alloy electroplated steel sheet
2) Two-layer zinc–iron alloy electroplated steel sheet
3) Organic composite-coated steel sheet

With their protective coating alloyed, applied in two layers or composited, these corrosion-resistant steel sheets have excellent corrosion resistance and pointability for relatively low coating weight. Their formability, weldability, and other properties are also balanced well. This report mainly describes the development concept and quality performance of each of the new types of corrosion-resistant sheets.

I. Introduction
Today, various types of zinc-coated steel sheets are used in large quantities to improve the durability of automobile bodies. Since zinc sacrificially protects steel from corrosion, one-side and two-side hot-dip galvanized steel sheets with relatively heavy coating weights, galvannealed steel sheets, electrolygelvanized steel sheets and organic-coated steel sheets with zinc powder, are commercially used in automotive body panels. These corrosion-resistant steel sheets, however, do not fully meet the application of high-strength steel sheets for weight reduction and deep-drawing steel sheets, cosmetic corrosion resistance, formability, weldability, and other, properties required of corrosion-resistant steel sheets for automotive use. Because of the electrochemical activity of zinc, electrolygelvanized steel sheets and hot-dip galvanized steel sheets are poor in wet adhesion of paint and are likely to cause blistering of the paint film. Organic-coated steel sheets and galvannealed steel sheets with heavy coating weights, have a tendency to take off from the coated surface and produce dents in panels during press forming. Organic-coated steel sheets and hot-dip galvanized steel sheets lack in spot weldability and are difficult to weld. Galvanized steel sheets also are inferior to cold-rolled steel sheets in appearance of the painted-coated surface and are narrow in the applicable range of high-strength steel sheets and deep-drawing steel sheets.

These problems might be solved by the use of zinc alloy electroplated steel sheets with lighter zinc or organic coatings and the development was pushed forth of zinc alloy electroplated steel sheets with high corrosion resistance for low coating weight. Three new types of corrosion-resistant steel sheets for automotive body panels have been developed as described below.

During the development work, basic research was carried out concerning the corrosion control mechanism of the autobody and the characteristics required of corrosion-resistant steel sheets for automotive use. Zn–Ni alloy electroplated steel (Zinklite—referred to as ZL), two-layer Zn–Fe alloy electroplated steel (Excelite—referred to as EL) and organic composite coated steel (Welcote-M—referred to as W2), as shown in Fig. 1 have been developed to satisfy various property requirements of carmakers.

These three new types of corrosion-resistant automotive sheet steels are described in the sections that follow, mainly with respect to their development concepts and performance characteristics.

II. Zn-Ni Alloy Electroplated Sheet Steel (ZL)

1. Development Concept

To secure formability and weldability, important properties for automotive body fabrication, it is desirable to produce corrosion resistant steel sheets by the electroplating process that does not change the mechanical properties of the base steel. To improve the anticorrosion performance of conventional electrolygelvanized steel sheets, however, it is necessary to increase the zinc coating thickness, which in turn decreases the weldability and press formability. The metallic coating to be deposited by the electroplating process, therefore, must meet the following requirements.

1) Raise the corrosion resistance of the coating layer above that of the zinc coating
2) Reduce the coating thickness and improve press formability and weldability

The designed conception of improving the corrosion resistance of electrodeposited metals based on the protective action of corrosion products of zinc in natural environments, which Okada had suggested in his study10 on the effects of alloying elements on the stabilization of Zn(OH)2 in neutral atmospheres.

From studies1–3) on the stability of synthetic Zn(OH)2 with various alloying elements, it was found that alloying elements, such as Al, Mg, Ni, Co and

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* Received March 24, 1983. © 1983 ISIJ
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Mn, retarded the change of Zn(OH)₂ to ZnO.

Based on this concept, nickel and cobalt were selected as alloying elements that can be electroplated and ZL, a steel sheet electroplated with a Zn–Ni alloy that contains cobalt, was developed. When establishing the composition of the actual alloy coating, the γ phase alloy was determined as the region of good balance resulted from various corrosion tests, as shown in Fig. 2. According to the measurements of corrosion potential and galvanic currents to cold rolled sheet in salt water, such a γ phase alloy has smaller potential differences with iron than that zinc has, and reduces the excessive protective action which prevents blistering and delamination of the paint film at the paint film defects and jointed portions with cold rolled sheet steel.

2. Quality Performance

1. Corrosion Resistance

ZL exhibits good paintability equivalent to that of cold-rolled steel and effectively prevents the occurrence of scabs and paint blisters. For this reason, ZL is used as two-side coated steel for not only the inner but also the outer panels of automobiles. Figure 3 shows the results of cyclic corrosion test conducted on actual doors with ZL sheet assembled into the door outer and coated with automobile paint. ZL was equivalent to galvannealed steel of heavy coating weight in perforation resistance.

The excellent corrosion resistance of ZL was also confirmed by the running test of actual automobiles on salt-covered roads. Photograph 1 shows the cosmetic corrosion at the lower front fenders after the running test that corresponds to five years. Chipping corrosion is adequately prevented.

2. Formability

Since it can retain the mechanical properties of the base steel, ZL can meet a wide range of property requirements from deep-drawing steel sheets to high-strength steel sheets, dual-phase steel sheets and highly bake-hardenable steel sheets. During press forming of body panels, ZL has less powdering and flaking than conventional hot-dip galvanized steel sheets, electrogalvanized steel sheets and zinc rich-paint-coated steel sheets and is easier to press form.
continuously. Since the Zn–Ni–Co coating is harder than zinc,5) the pickup of the coating by forming dies is lessened and since the coating is higher in melting point than zinc5) the buildup of coating metals on the die is prevented.

It was confirmed by continuous press forming on an actual press line that ZL sharply reduces the occurrence of dents and other forming defects as compared with electrogalvanized steel sheets.

Since ZL can eliminate in this way time and labor for the maintenance of press forming dies and the repair of defects in formed parts, it is evaluated as corrosion resistant sheet steel for automotive bodies suited for the introduction of automatic presses and the saving of labor in press forming.

3. Weldability

In continuous spot welding, ZL causes less electrode wear and thus, provides better as-finished appearance and permits more weld spots to be made continuously than electrogalvanized steel sheets and galvannealed steel sheets. Since the melting point of the coating is higher than that of electrogalvanized sheet steel, the welding current flows over a shorter path and concentrates in a smaller area. And because the electric resistance of the coating is lower than that of galvannealed sheet steel, less heat is generated at the interface between the electrode and the sheet. Thus, electrode wear due to the alloying of the electrode material with the coated metal at the electrode surface is considered to be alleviated. The difference in ohmic resistance of the coating can be explained as the difference in the amount of surface oxides.5)

The appearance of electrodes after continuous series spot welding is shown in Photo. 2. ZL causes the second least electrode wear after cold-rolled sheet and can lessen the replacement and dressing frequencies of the electrode tip. By reason of this good weldability, ZL is evaluated as corrosion-resistant steel sheet adapted for the introduction of welding robots and the production of components that involve the lap welding of three sheets.

3. Manufacturing Technology4)

The electrodeposition of a Zn–Ni alloy from a relatively simple bath like a sulfate bath results in an anomalous codeposition. To control the composition of the alloy coating constant, it is necessary to clarify the relationship between electroplating conditions and coating composition. According to the operation analysis results of a continuous electroplating line, the introduction of computer control was found to be effective, because many operating factors affect the composition of the coating.

Accordingly, software and hardware required for computer control were developed and the system schematically illustrated in Fig. 4 was completed. Operation control by the system can reduce the variations in coating weight and nickel concentration in the coating to sufficiently low levels.

III. Two-layer Zn-Fe Alloy Electroplated Steel Sheet (EL)

1. Development Concept

In recent years, corrosion-resistant steel sheets for automotive use have been increasingly required to withstand cosmetic corrosion as well as perforation corrosion, and two-side zinc-coated steel sheets have been adopted in the outer panels of automobile bodies, too. Now that cathodic electrodeposition system has established itself, the paintability of zinc-coated surfaces has come to be emphasized more than ever.

Galvannealed steel sheet had excellent underfilm corrosion resistance6,7) and is a proven material for perforation resistance. When to be used electroplated with primer for the outer surfaces of the autobody, however, it has such problems that it is likely
to cause craterform paint film defects during cathodic electrodeposition and does not easily accept the cathodic electrodeposition paint system. The two-layer Zn–Fe alloy electroplated steel sheet EL has been developed to combine the perforation resistance of galvannealed steel sheets with the mechanical and surface chemical properties of cold-rolled steel sheets by use of the electroplating process.

During the development work, a detailed study was made of the relationship between the composition of the Zn–Fe alloy coating and properties required of the corrosion-resistant steel sheets for automotive use. The perforation resistance of EL electroplated with Zn–Fe alloys of different iron contents and electrodeposited with cathodic primer was determined by salt spray test. The test results are given in Fig. 5. The Zn–Fe coating has good perforation resistance over an iron content range of 10 to 30 % and favorably compares with galvannealed steel in performance. In this iron content range, Zn–Fe coating consists of the α and γ phases and does not contain the η phase, as was confirmed by X-ray diffraction analysis. Some authors have attributed the d value of 2.10 Å to η phase.8 But η phase has a main peak with d value of 2.47 Å as is clearly seen in the top chart of Fig. 6. Other 3 charts of Fig. 6 do not show 2.47 peak, which means that Zn–Fe alloy coatings of thin concentration range do not contain η phase. Due to the lack of η phase, delamination of the paint film, a phenomenon often observed in conventional zinc-coated steel sheets, is retarded. And the perforation resistance is also better than that of zinc-coated steel (Fig. 5). An iron content of over 30 % is not desirable, because the coating does not offer enough sacrificial protection for the base metal in that case.

Conventional zinc-coated steel sheets do not readily develop scab corrosion and in this respect, are effective materials against cosmetic corrosion. In wet environments, however, they do not tightly hold paint and lack in applicability for anti-cosmetic use. There-
fore, the relationship between the iron content of the Zn–Fe alloy coating and the wet adhesion of the paint film was investigated. The results are given in Fig. 7, which shows that the wet adhesion of the paint film improves as the iron content of the coating exceeds 60%. Delamination of the paint film in wet environments chiefly occurs at the interface between the electrodeposited cathodic paint and the phosphate coating. The formation of phosphophyllite, a type of phosphate coating, is difficult to dissolve in alkali generated during cathodic electrodeposition and under corrosive environments is reported to be effective in retarding this delamination. As a phosphate coating is applied by dipping, the phosphate coating almost entirely consists of phosphophyllite on the Zn–Fe alloy when the iron content exceeds 60%.

One problem encountered when conventional zinc alloy coated steel sheets are used for the outer surfaces of the automobile bodies is the occurrence of craterform paint film defects during electrodeposition. Application of intermediate and top coats over such primer film with defects cannot improve the appearance of the car body. The relationship between the cratering tendency during cathodic electrodeposition and the iron content of the Zn–Fe alloy coating is presented in Fig. 8, which indicates that cratering can be reduced when the iron content is 60% or more.

It is obvious from the above-mentioned experimental findings that there is no single Zn–Fe alloy coating that can simultaneously meet all of the four quality properties required of automotive anticorrosion steel sheets. A zinc-rich coating provides good resistance to perforation and scab corrosion, while an iron-rich coating prevents cratering during cathodic primer electrodeposition and ensures good wet adhesion for the paint film. When account is taken of the fact that the later properties are surface properties, a two-layer Zn–Fe alloy coating with a lower layer of corrosion-resistant zinc-rich coating and an upper layer of thin iron-rich coating can meet all of the property requirements. Based on this concept, the two-layer Zn–Fe alloy electroplated steel sheet, has been developed. When the coating weight of the upper layer is 2 g/m² or above a phosphate film uniformly composed of phosphophyllite can be formed to impart good wet adhesion and prevent cratering during cathodic electrodeposition. The iron content of the upper layer was set at a range of 75 to 85% by considering quality performance and minimization of the corrosion potential difference with the lower layer. The iron content of the lower layer was designed at a range of 10 to 20%.

2. Quality Performance

1. Paintability and Corrosion Resistance

One characteristic of EL is that it is a corrosion-resistant steel sheet that can be applied for the outer panels of the automobile body to ensure protection from cosmetic corrosion. One property requirement is good wet adhesion for the paint film. EL exhibits excellent wet adhesion without chromate sealing, because the phosphate coating is converted to phosphophyllite by the upper layer of the Zn–Fe alloy coating.

Another requirement is the capability to prevent cratering during the application of current for cathodic paint electrodeposition. Figure 9 shows the relationship between the cathodic paint electrodeposition conditions and the appearance of the paint film. EL provides paint films of good appearance for relatively high applied voltage and short electrode distance. Approximately the same wide range of electrodeposition conditions as for cold-rolled steel sheets can be applied. This characteristics is not found in conventional zinc-coated steel sheets.

The effect expected of Fe–Zn alloy coated steel is corrosion resistance imparted by the cooperative ac-
tion of the alloy coating and the paint film. Paint-electrodeposited sheets with cross cut in the paint film, by considering unpainted exposed areas and contact corrosion, were evaluated for perforation resistance by the combined corrosion test that involved salt-spray, wet and dry environments. The perforation resistance of EL with a coating weight of 20-3 g/m² is almost equal to that of galvannealed steel with a coating weight of 45 g/m². In particular, EL electrodeposited with only 10 μm of cathodic paint exhibits good perforation resistance, probably because it can readily accept the cathodic electrodeposition paint.

2. Formability
Since press formability depends on the nature of the base metal, EL is identical to corresponding cold-rolled steel in press formability.

In press forming, the alloy coating of EL peels not as flakes but as powder, like galvannealed steel sheets. Photograph 3 compares the condition of powder adhering to parts stamped on a model press as determined by tape test. Powdering of the EL coating is extremely slight as compared with galvannealed steel. The reason is probably as follows: The lower layer of EL is a uniform coating composed of δ and ε phases and is free from weak points subject to stress concentration, whereas the coating of galvannealed steel is lamellar in structure and is critical between the δ₁ and ε phases. Separation between the upper and lower layers was not observed in EL.

3. Weldability
As for optimum spot welding conditions, EL is approximately the same as galvannealed steel sheets in welding conditions and is weldable over a sufficiently wide range of conditions. Figure 10 gives the results of electrode life test. EL can be continuously welded for over 5,000 spots with the same pair of electrodes. This good spot weldability may be ascribed to the fact that the Zn-Fe alloy coating has a suitable amount of resistance and does not contain the γ phase that easily reacts with the electrode material.

3. Manufacturing Technology
EL is manufactured by using the anode center injection cell. This cell is adopted because making the flow speed through the cell as uniform as possible for both sides of strip is of particular importance to homogenize the composition of the Zn-Fe alloy coating and because operation with high current density is possible. The upper layer of coating is continuously applied after the lower layer. The coating weight of each of the upper and lower layers and the composition of the Zn-Fe alloy can be simultaneously measured in a short time by glow discharge spectroscopy. The measurement results are fed back to ions supply system linked with a process computer, enabling the manufacture of EL products with stable quality.

IV. Organic Composite-coated Steel Sheet (W2)
1. Development Concept
Today, galvanized steel and zinc primer coated sheet (Zincrometal—referred to as ZM) are widely used as coated steel sheets for corrosion protection of automobile body. Galvanized steel is superior to ZM in formability and weldability, but has such problems as the rapid consumption of zinc under specific corrosive environments and the low applicability in cathodic electrodeposition paint. ZM, on the other hand, exhibits stable corrosion resistance in the form of flat sheet and for this reason, is predominantly used in Europe and the United States, but is likely to cause galling and paint film peeling during press forming, resulting in the drop in corrosion resistance of formed areas. Both types of coated steel sheets have the com-
mon problems that formability and weldability deteriorate when the coating weight is increased to improve corrosion protection. Electrogalvanized sheet with zinc rich paint2 (Welcote—referred to as WC) is an alternative material to make up for the disadvantages of ZM. To meet customers’ requirements for better corrosion protection, formability and weldability, an organic composite-coated steel sheet W2 has been developed. It has a special, improved zinc-rich paint applied on an alloyed zinc coating of low coating weights.

The high corrosion resistance of ZM is derived from the combined effect of the passivation layer (Dacromet) that utilizes the corrosion protection of chromate and the zinc pigmented primer layer (Zincromet) that is a zinc-rich paint coated upper layer. W2 in contrast, consists of an undercoat of Zn-Ni alloy that corresponds to the passivation layer and offers excellent corrosion resistance and formability, an intermediate coat of chromate applied to improve paint adherence and corrosion resistance, and a top-coat of special zinc-rich paint with hard and conductive metal powder14 added to enhance both weldability and paint film formability. The thickness of this paint film is 5 μm and one half of or less than that of the zinc pigmented primer layer. W2 is equal to or better than ZM in corrosion resistance, because an alloy coating of high corrosion resistance is applied as the lower layer although the paint film in the upper layer is thinner, and provides far higher formability and weldability.

2. Quality Performance

1. Corrosion Resistance

The corrosion resistance in the unpainted condition depends on the corrosion resistance and thickness of the upper organic composite coating and the lower Zn-Ni alloy coating. Figure 11 shows the relationship between the film thickness and corrosion resistance determined by the combined cyclic corrosion test method14 that is considered the best method to evaluate the corrosion resistance of automotive body panels. As evident from the diagram, the organic composite coating has two effects: delaying the start of sheet thickness reduction and decreasing the corrosion rate. For ZM, the start of sheet thickness reduction by corrosion is early but the rate of subsequent corrosion is low, because the paint film is applied to a large thickness of 17 to 21 μm. With WC, on the other hand, the sheet thickness reduction starts as soon as the zinc coating is consumed, because the upper organic composite coating is thin. For this reason, the durability of the paint film has been improved by lowering the consumption rate by use of the Zn-Ni alloy coating and by decreasing the amount of zinc in the organic coating. As a result, W2 is provided with higher corrosion resistance than ZM, even when the thickness of the organic composite coating is reduced to 5 μm.

W2 also has excellent corrosion resistance in the painted condition and in formed areas. Photograph 4 shows the corrosion of specimens cut from the heavily worked portions of press-formed rear wheel house outer panels and tested by the combined cyclic corrosion test. Figure 12 shows the sheet thickness reductions of hood ridges measured under the combined cyclic corrosion test. While the ZM has corrosion resistance reduced by press forming, as compared with Fig. 11, W2 has a smaller drop in corrosion resistance. This difference can be explained as follows: In the case of ZM, the lower layer is destroyed by press forming, resulting in peeling of the paint film, whereas in the case of W2, galling and paint peeling occur less on the upper organic composite coating and the Zn-Ni alloy coating exists below.

2. Formability

ZM has zinc powder added 85 % by volume to the epoxy-based resin to ensure good weldability and corrosion resistance. This high zinc powder content, however, is likely to cause paint powdering, galling or peeling in heavily worked portions during press form-
ing. To improve formability, W2 has the total metal powder content limited to 75% or less by adding hard and conductive metal powder. Figure 13 comprehensively evaluates the formability of coated steel sheets by round and rectangular shell drawing tests and shows that W2 is formable better than ZM. The chromate coating also contributes to this good formability by enhancing the adherence of the organic composite to the base steel.

3. Weldability and Adhesive Joinability

The largest problem with organic coated steel sheets when they are used as corrosion-resistant materials for automobile bodies is weldability. Decreasing the thickness of the organic coating is effective in decreasing electric resistance by the paint film and electrode contamination by the organic matter. Since it contains a hard metal powder of good conductivity and has an organic composite coating thickness of only 5 μm, W2 is more weldable than ZM although its metal powder content is lower.

Figure 14 shows the optimum spot welding current ranges of W2, ZM and cold-rolled steel and Fig. 15 gives their continuous spot weldability test results. W2 is superior to ZM in spot weldability.

When assembling automotive body panels, structural adhesives, including sealers, are used in large quantities as jointing means other than welding. Adhesive joinability is an important property for corrosion-resistant steel sheets, too. Since the passivation layer is low in resin content, ZM ruptures in that layer when shear tested by use of adhesion specimens and is low in strength as shown in Table 1. W2 does not peel in the adhesive-jointed surfaces, withstands the test load until the rupture of the steel sheet and exhibits high performance equivalent to that of cold-rolled steel, because the upper and lower layers are both strongly adherent.

3. Manufacturing Technology

W2 is now manufactured by the combined use of existing electroplating and painting lines. The principal characteristic of its manufacturing technology lies in the thin-film application of the Zn-Fe alloy and metal powder-containing paint. A special coating control system is developed for W2.

V. Conclusion

As new types of corrosion-resistance steel sheets for automotive use, the Zn-Ni alloy electroplated steel sheet, two-layer Zn-Fe alloy electroplated steel sheet and organic composite-coated steel sheet have been developed. Each offers excellent resistance to the cosmetic corrosion and perforation of automotive body panels. The protective coatings of these corrosion-resistant steels are based on zinc that has a sacrificial protection effect on steel and although thin, are provided with good corrosion resistance and paintability by alloying, multiple layering or compositing. The low coating weights impart good formability and weldability, thus ensuring well-balanced properties required of automotive body panels. Since the protective coatings are applied by the electroplating process that exerts no thermal effect, the new corrosion-resistant steels can freely select mechanical properties from those of deep-drawing steel to those of high-strength steel. The quality characteristics of these three types of corrosion-resistant steel sheets for automotive body panels may be summarized as follows:

1) Zn-Ni Alloy Electroplated Steel Sheet

Electroplated with the γ phase of the Zn-Ni alloy,
ZL has excellent corrosion resistance in the unpainted condition and improved paint adhesion due to suppression of galvanic action of zinc in saline environment. The excellent corrosion resistance of ZL was confirmed by corrosion tests on body parts and automobile running tests on salt-covered roads. ZL also has good continuous weldability and formability and is an ideal, general-purpose automotive corrosion-resistant steel sheets with well-balanced properties.

(2) Two-layer Zn–Fe Alloy Electroplated Steel Sheet

EL is a steel sheet electroplated with two Zn–Fe alloy layers, the iron content being 10 to 20% in the lower layer and 75 to 85% in the upper layer. The two-layer Zn–Fe alloy coating provides EL with corrosion resistance equivalent to that of galvannealed steel sheet and paintability equivalent to that of cold rolled sheet. Especially, when electrocoated with cationic electro-primer, EL is quite free from cratering. This new type of corrosion-resistant steel for automobiles also has better formability and weldability than galvannealed steel.

(3) Organic Composite-coated Steel Sheet

With a chromate layer and special paint containing conductive metal powder applied on a Zn–Ni alloy electroplated steel sheet, W2 is superior to ZM in corrosion resistance, formability and weldability. High corrosion resistance in the unpainted condition and press-formed portions are the main features that make W2 a suitable corrosion-resistant material for automotive use.

REFERENCES


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