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Progress in Precoated Steel Sheets for Automotive Use

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Progress in Precoated Steel Sheets for Automotive Use*



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In the light of these developments, recent developments in organic composite coating (thin organic resin/Zn-Ni alloy), galvanized steel with anti-powdering qualities and ultra-fine alumina dispersed Zn-Co-Cr-Al₂O₃ electroplating are described in this paper.

1 Introduction

The problem of corrosion of automobile bodies caused by road deicing salts and sea salt has led to a major shift in materials for auto body production, from conventional cold-rolled steel sheets to precoated steel sheets.

To enhance the corrosion resistance of automobile bodies, automakers have altered body designs and improved phosphating and painting techniques. Improved techniques include not only wax injection and the use of sealants, but also dip-type phosphating and cathodic electropainting instead of the conventional spray type phosphate treatment and anodic electropaint methods. Chipping-resistant paints have also been adopted. However, because the use of precoated steel sheets has proved effective, the number of automotive parts made of this material has increased yearly, until more than 50% of the typical auto body part is now made of precoated steel.

In the 1970s, corrosion of auto bodies became an issue for reasons of safety and durability. With corrosion generally originating at joints and closed structural parts, emphasis was laid on the prevention of perforation corrosion of inside parts. One-side coated steel sheets were used adequate to meet this need, but in recent years, great importance has also been attached to the prevention of rusting of the exposed side of outer panels caused by chipping, leading to the adoption of two-side coated steel sheets.

Precoated steel sheets for automotive applications must provide not only excellent corrosion resistance, but also good performance in the fabrication and painting processes. Necessary properties include press formability, weldability, phosphatability, and paintability. To meet these requirements, Kawasaki Steel has developed a series of new precoated steel sheets, including Zn-based coated steel sheets and prepainted steel sheets.

Individual automakers apply a wide range of rust prevention and material property specifications to precoated steel sheets for automotive use. Priorities are set on the basis of both manufacturing requirements and market needs, and materials are selected in consideration of the specific advantages offered by the respective types of precoated products. Electrogalvanized steel sheets with relatively heavier coatings are used in Europe and America, for example, while Japanese automakers tend to prefer Zn-Ni and Zn-Fe alloy electroplated steel sheets which offer high corrosion resistance at lower coating weights. Japanese automakers also use double-layered electroplated steel sheets with an upper layer of Fe-P plating, which provides the same phosphatability and paintability as cold-rolled steel sheets.

Automakers have recently begun to use Zn-Ni alloy electroplated steel sheets with a thin organic film of about 1 μ m, galvanized steel sheets with improved powdering resistance, and double-layered galvanized steel sheets with an upper layer of Fe-P.

This paper presents major recent developments in

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precoated steel sheets for automotive use from a historical viewpoint, covering a wide variety of products from one-side electrogalvanized sheets to recently developed ultrafine alumina dispersed Zn-Co-Cr-Al₂O₃ electroplated sheets.

2 Development of Zinc-Alloy Electroplated Steel Sheets

2.1 One-Side Galvanized Steel Sheets

The excellent corrosion resistance of galvanized steels is a result of a phenomenon known as sacrificial protection, in which the zinc coating preferentially dissolves to form corrosion products which protect the steel substrate. Galvanized steel is used in a wide variety of applications, including building materials, where good corrosion resistance is required, and heavy coating weights of 70 g/m² or more are necessary to meet the rust prevention requirements of automotive applications. On the other hand, heavier coating weights are disadvantageous in terms of weldability, paint adhesion, and paint appearance, all of which are important factors in auto body manufacture. Two-side galvanized sheet is generally not used in the exposed panels of the auto body, where these factors are involved, thus requiring the development of techniques for the production of one-side galvanized products.

Two methods are used in producing galvanized steel sheets, the hot-dip galvanizing process and the electrogalvanizing process. Kawasaki Steel formerly produced only two-side galvanized steel sheets, but during the 1970s began to develop new methods of coating only one side of the steel sheet. For hot-dip galvanizing, the company developed a method in which opposite-side coating with a minimal weight coating is mechanically removed with a grinder. Subsequently, in 1981, the company introduced a unique method of producing one-side hot-dip galvanized steel sheets. Called stop-off coating (SOC), this method is characterized by the use of a removable stop-off agent.¹⁾

The stop-off agent used in SOC is composed of sodium silicate, sodium borate, magnesium oxide, titanium oxide and aluminum oxide, and is applied to one side of the sheet using a roll coater before annealing in the continuous hot-dip galvanizing line. The agent vitrifies during annealing to form a dense film which completely prevents zinc deposition in the zinc bath, as well as contact of the covered steel surface with air. After plating, the film is easily removed by repeated bending using multiple small-diameter rolls, which gives a one-side galvanized steel sheet. SOC has also been applied to the production of one-side galvanized steel sheets,²⁾ since the properties of the glassy film do not change upon galvannealing after hot dipping and bluing of the uncoated surface does not occur.

It is relatively easy to produce one-side heavier elec-

trogalvanized steel sheets with coating weights of 70 g/m² and more. Kawasaki Steel has established techniques for producing one-side heavier coated steel sheets which employ horizontal cells. In this method, zinc deposition on the uncoated surface and edge overcoating are prevented, electrolyte flow rate is improved, and a uniform coating weight is ensured.³⁾ In 1982, a radial-cell type electrogalvanizing line was constructed at Chiba Works.⁴⁾ In the radial cell, the strip is coated while passing around a large-diameter conductor roll; contact between the electrolyte and the reverse side of the strip is not possible, preventing zinc deposition on this "second" side of the strip. The chloride bath adopted for plating ensures good conductivity and current density is high, and accordingly, coating uniformity is excellent. Thus, the efficient production of high-quality one-side galvanized steel sheets has been realized in commercial operation.

2.2 Zinc-Alloy Electroplated Steel Sheets

In order to use galvanized steel sheets with heavier coating weights as auto body material, higher capacity welders are necessary. Other disadvantages of heavier galvanized steel sheets are inferior continuous spot weldability and susceptibility to blisters after painting, which results from the great difference in corrosion potential between the zinc coating and the steel substrate. Further, wet adhesion after three coats is not good, and microdefects called pimples occur during press forming. The various problems particularly affected the Japanese automobile industry where automated welding robots are of small capacity, and chromate sealing is not conducted after phosphate treatment. Thus problems suggested the need for lighter coatings with high corrosion resistance. To meet this need, Kawasaki Steel developed a Zn-Ni alloy electroplated steel sheet (**RIVER HI-ZINC**)⁵⁾ and Zn-Fe alloy electroplated steel sheets⁶⁾.

Zn-Ni alloy plated steel sheets show excellent corrosion resistance when the nickel content of the coating is 10 to 16%.⁷⁾ Coatings with nickel contents in this range have a γ single phase layer, and local microcells do not form in the coated layer. Further, a corrosion product mainly composed of zinc hydroxide is produced; this compound exhibits a protective effect due to the low conductivity and suppression of the oxidation-reduction reaction at the surface of the coating. These characteristics are considered to account for the excellent corrosion resistance of Zn-Ni alloy plated steel sheets.⁸⁾ **Figure 1** shows results of the corrosion resistance of steel sheets with cathodic electropaint 5 μ m in thickness, which was conducted to determine the applicability of materials to use in parts where electropainting is difficult. A Zn-Ni alloy plated steel sheet with a coating weight of only 20 g/m² is equivalent or superior to galvanized steel sheet with a coating weight of 90 g/m². The continuous spot weldability of the Zn-Ni alloy plated

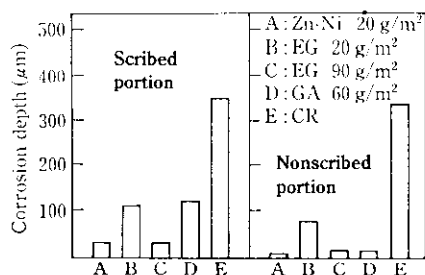


Fig. 1 Corrosion depth of various pre-coated specimens with 5 μm cationic electrodeposition painting after 2500 h salt spray test⁵⁾

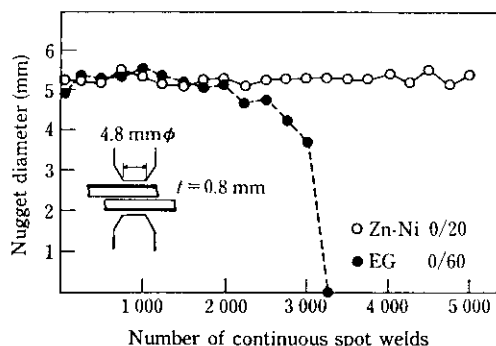


Fig. 2 Continuous spot weldability of Zn-Ni alloy-electroplated steel and electrogalvanized steel⁵⁾

steel sheet is shown in Fig. 2. Weldability improved substantially because of the lighter coating weight and because nickel has a high melting point. For these reasons, this type of steel sheet has been adopted widely in Japan.

Galvannealed steel sheets have been used as inner panels because of their excellent corrosion resistance after painting, as shown in Fig. 1. However, since products of the hot-dipping process are inferior in base steel properties, surface appearance, and coating weight uniformity, Kawasaki Steel studied the feasibility of using Zn-Fe alloy electroplated steel sheets in automotive body applications.

Since Zn-Fe alloy plated steel shows good corrosion resistance when the Fe content of the film is 10 to 20%, it is necessary to control Fe content in this range. In the conventional sulfate bath, the Zn-Fe alloy plating, similar to Zn-Ni alloy plating, is known to be subjected to anomalous codeposition,⁹⁾ in which electronegative Zn^{2+} ions deposit preferentially, and it is necessary that the proportion of Fe^{2+} ions in the plating bath be higher than that of Zn^{2+} . The cathode efficiency is different from the anode efficiency, necessitating the use of insoluble anodes and the external supply of ions by chemical means in order to maintain a constant electrolyte composition. There is no problem with the use

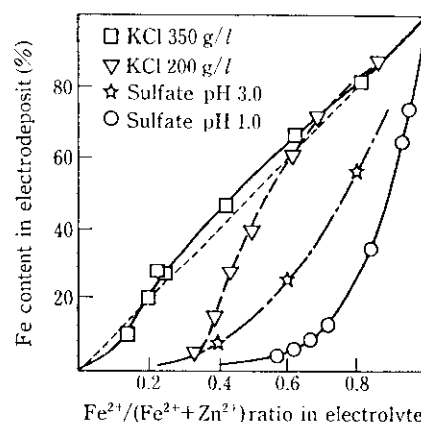


Fig. 3 Effect of electrolyte composition on Fe content in Zn-Fe alloy electrodeposit⁶⁾

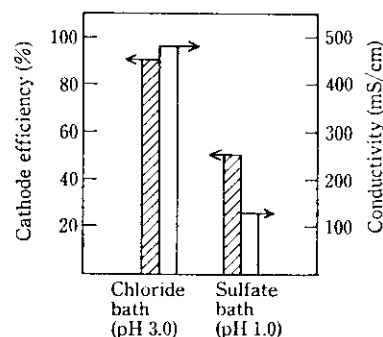


Fig. 4 Effect of electrolyte solution on cathode efficiency and conductivity⁶⁾

of insoluble anodes in Zn-Ni alloy plating, but in Zn-Fe alloy plating the Fe^{2+} ions in the bath are oxidized and transformed into Fe^{3+} ions by oxygen generated from the anode. It is necessary to install an Fe^{3+} ion reduction device because an increase in Fe^{3+} ions in the bath poses various problems such as poor surface appearance, unstable Fe content in the coated layer, and decreased cathode efficiency.

At the electrogalvanizing line at Chiba Works, zinc plating is conducted using a chloride bath and soluble anodes. An examination was made as to techniques for alloy plating using a chloride bath in order to facilitate electrolyte exchanges. As shown in Fig. 3, it was found that equilibrium codeposition, in which the Fe^{2+} ion and Zn^{2+} ion ratio in the electrolyte is almost the same as that, in the electrodeposit, can be accomplished by increasing the KCl concentration of the supporting electrolyte agent. Further, because the cathode efficiency is above 90%, as shown in Fig. 4, the electrolyte composition can be easily controlled with soluble anodes. With an increase in the concentration of the supporting electrolyte agent, as shown in Fig. 5, the Fe content of the film becomes independent of the current density and the electrolyte flow rate and stable Fe

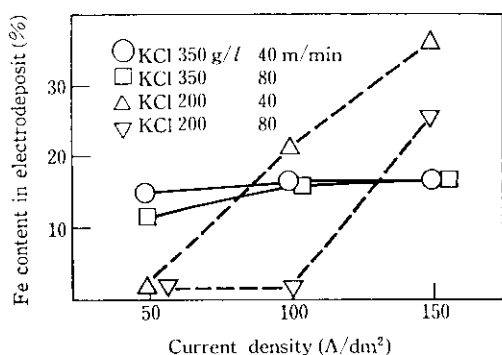


Fig. 5 Effect of current density, KCl concentration and flow rate on Fe content in Zn-Fe alloy electrodeposit⁶⁾

contents can be obtained over a wide range of current densities. When Zn-Fe alloy plated steel sheets are produced using a sulfate bath, very sophisticated techniques are required to achieve proper electrolyte composition control, reduction from Fe^{3+} ions to Fe^{2+} ions, uniform electrolyte flow rate, and stable Fe content. It was found that in the chloride bath Fe^{3+} ion-reduction device was unnecessary and that plated steel sheets can be produced relatively easily and efficiently. Kawasaki Steel applied this technique to the production of Zn-Ni alloy plated steel sheets¹⁰⁾ and established mass production technology for Zn-Fe and Zn-Ni alloy plated steel sheets using a chloride bath and soluble anodes.

2.3 Double-layered Zinc-Alloy Electroplated Steel Sheets

Since satisfactory prevention of perforation corrosion is now possible by using galvanized steel sheets and alloy plated steel sheets, measures to prevent cosmetic corrosion are now a focus of attention among automakers, with a strong need being felt for the application of precoated steel sheets to exposed outer panel surfaces.

Zinc-based coated steel sheets when applied to the exposed side of outer panels must provide paintability and paint adhesion equivalent to those of cold-rolled steel sheets. It was found that when zinc-based coated steel sheets are processed at high voltage during cathodic electropainting, a paint defect called cratering occurs, and wet adhesion after three coats (consisting of cathodic electropaint, sealer coat, and top coat) are inferior. The cause of cratering is thought to be as follows: when the surface properties of the steel sheet are non-uniform, electropainting current becomes concentrated locally in the initial stage of electropainting, and paint quality deteriorates due to the heat generated by electrical discharge.¹¹⁾ The resultant defect appears as concavities or pinholes, and is easy to occur in Zn-Fe alloy plated steel sheets, although not in pure-zinc coated

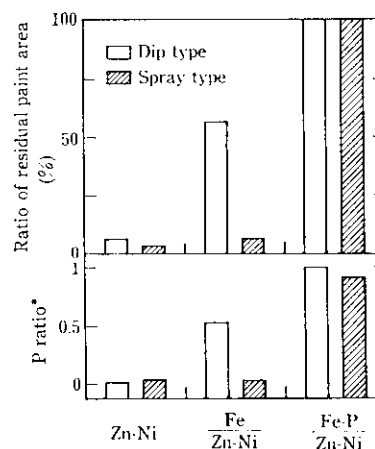


Fig. 6 Effect of Fe-P upper coating on phosphatability and wet adhesion of double layered Zn-Ni alloy-electroplated steel (*P ratio = phosphophyllite/(phosphophyllite + hopeite))⁵⁾

steel sheets.

Wet adhesion is evaluated by immersing a coated steel sheet after three coats in hot deionized water at 40°C for ten days and conducting a cross-cut peeling test using tape immediately after the specimen is taken from the water. This deterioration of wet adhesion posed a special problem in Japan, where automakers do not generally use chromate sealing.

Considering the fact that these paint defects and paint peeling problems do not occur with cold-rolled steel sheets, Kawasaki Steel investigated the application of an Fe-based plating to Zn-Ni or Zn-Fe alloy plated steel sheets. As shown in Fig. 6, perfect performance is not realized with the Fe plating, but the *P* ratio (phosphophyllite/phosphophyllite + hopeite) of the phosphate film and wet adhesion improved markedly with Fe-P plating. Although the phosphorus content of the Fe-P plating is very low, below 0.5%, the added phosphorus promotes the dissolution of Fe during phosphate treatment and increases initial phosphate crystal nuclei, with the result that a film of closely-packed phosphophyllite ($\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) is formed. In general, wet adhesion is strongly affected by the quality of the phosphate film and improves as the *P* ratio increases (i.e. when a greater proportion of phosphophyllite is present in the film). This is because the phosphate coating consists of phosphophyllite is less soluble in alkaline solutions than hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$).¹²⁾

The effect of the Fe-P coating weight on cratering is shown in Fig. 7. When the coating weight of the Fe-P upper layer is 2 g/m² or more, craters do not form even at an applied voltage of 350 V; thus, cratering is effectively suppressed at this coating weight. Results of an investigation of the cratering resistance of various precoated steels are shown in Fig. 8. Cratering is rare in

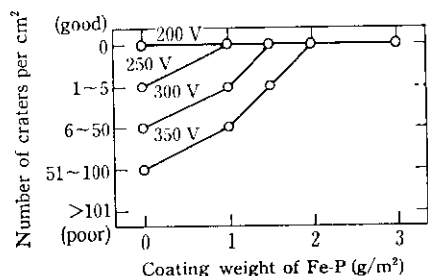


Fig. 7 Effect of coating weight of Fe-P on number of craters (on Zn-Ni lower layer)¹³⁾

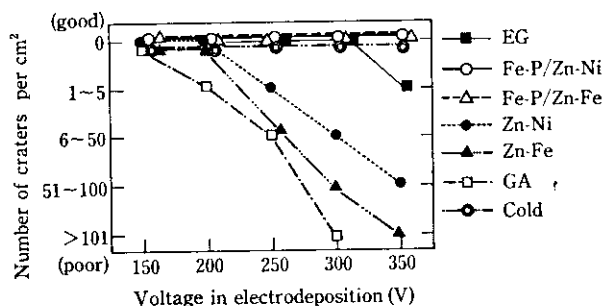


Fig. 8 Relation between paintability (number of craters) of various precoated steels and charge voltage in cathodic electrodeposition

pure-zinc plated steel sheet, but occurs with considerable frequency in Zn-Fe alloy plated steel sheet, even at relatively low voltages. However, craters do not form even at 350 V with double-layered alloy plated steel sheets with an Fe-P upper layer, which possess a cratering resistance comparable to that of cold-rolled steel sheets.

An adverse effect of the Fe-P coating in the upper layer on corrosion resistance was initially feared, but the coating weight of the Fe-P layer is light at 2 g/m², the layer dissolves to a considerable extent during phosphate treatment, and the remained Fe-P is protected by the sacrificial effect of underlying Zn alloy layer. Double-layered alloy plated steel sheets are less susceptible to red rust initiated in scratched parts and show the same performance as the underlying alloy plating with respect to thickness reduction.¹³⁾

Double-layered Fe-P/Zn-Ni alloy plated steel sheets (**RIVER HI-ZINC SUPER**) and double-layered Fe-P/Zn-Fe alloy plated steel sheets (**RIVER EX ZINC**) are used in exposed automotive panels because they provide the same phosphatability and paintability as cold-rolled steel sheets.

Wet adhesion is considered very important from the standpoint of paint adhesion and corrosion resistance after painting in both inner and outer automotive parts, and many studies have been conducted.¹⁴⁻¹⁶⁾

Researchers have found that wet adhesion is good

even in the hopeite film when the phosphate crystal size is small. The adverse effect of hopeite on wet adhesion is explained by the fact that 4H₂O in the hopeite film dehydrates during curing and converts into 2H₂O, but reconverts to 4H₂O during dipping.¹⁴⁾ As a solution to the problem of wet adhesion of Zn-based plated steel sheets, a phosphate solution to which Ni²⁺ ions and Mn²⁺ ions are added was developed.^{15,16)} Various opinions also exist on the cratering which occurs during cathodic electropainting. Cratering depends generally on electropaint conditions, and has improved considerably with the development of high-build cationic electropaints represented by Uniprime.¹⁷⁾ High-build cationic electropaints combine large film thicknesses and high throw power with low solvent contents¹⁸⁾, and are effective in preventing cratering, although they were not originally developed for this purpose.

Owing to these improvements in phosphate solutions and electropaints, Zn-Ni alloy plated steel sheets in which cratering is less common than in Zn-Fe alloy plated steel sheets are, in many cases, used without Fe-P plating for exposed panels of the automotive body. On the other hand, poor paint appearance of the precoated steel sheets, although initially considered a problem, can be avoided by the use of improved painting techniques. The quality levels now possible are demonstrated by the use of precoated steel sheets as the base steel in products where distinctness of image after painting is an important feature. The current state of the art is represented by LASERMIRROR,¹⁹⁾ a premium grade automotive sheet developed by Kawasaki Steel.

3 Development of Thin Organic Composite Coated Steel Sheets

3.1 Weldable Prepainted Steel Sheets

For use in applications where resistance to perforation corrosion is required, as with one-side galvanized steel sheets, steel makers have, for example, developed a weldable zinc-rich primer steel sheet. A typical example is Zincrometal²⁰⁾, developed by Diamond Shamrock (Kawasaki Steel began production of this product under license in 1976.²¹⁾). Zincrometal is obtained by applying a chromic acid coating containing zinc powder (Dacromet) in a thickness of about 2.5 μm to a cold-rolled steel sheet, and baking on a special epoxy resin-based zinc-rich paint (Zincromet) which is further applied to the Dacromet layer. The total film thickness of the Zincrometal coating is about 15 μm. Kawasaki Steel developed a **KZ** coated steel sheet which is phosphated instead of being treated in chromic acid based on its own technology. Since these steel sheets are pre-painted, they are effective in preventing perforation corrosion in parts where electropaint is difficult to apply, and have been widely used in Japan as well as in Europe and America.

Disadvantages of these prepainted steel sheets were pointed out, however, when they were introduced. For example, the film is susceptible to flaking off during press forming, resulting in pimples on the surface of formed parts. In addition, electrode life in spot welding is short and continuous spot weldability is bad. Further, the corrosion resistance of these prepainted steel sheets is provided mainly by the barrier effect, in which the film seals out oxygen and water, rather than by sacrificial protection. This fact is important because the protection of damaged areas and edge portions, generally effected by sacrificial protection, was insufficient, and improvement was therefore required.

3.2 Organic Composite Coated Steel Sheets

To eliminate the drawbacks of Zincrometal, attempts were made to reduce the thickness of the organic film by using a precoated steel sheet substrate rather than cold-rolled steel sheets. Kawasaki Steel developed an organic composite coated steel sheet (ZINCROMETAL K II) in which a Zn-Ni alloy plated steel sheet is used as the base steel, a Dacromet coat is applied to this steel, and a Zincromet coat with a film thickness half the conventional thickness is baked onto the Dacromet coat.²²⁾

To provide lubricity, 0.4% MoS₂ is added to the Zincromet film of Zincrometal K II; 4% ZPC (K₂O · 4CrO₃ · 4ZnO · 3H₂O) is also added to improve corrosion resistance. Zincrometal K II is a great improvement over Zincrometal in terms of the resistance of the film to damage during press forming, flaking, corrosion resistance, and weldability. The continuous spot weldability of Zincrometal K II is shown in Fig. 9. Welding is no longer possible at 3 000 spots in Zincrometal, while in Zincrometal K II, continuous spot welding is possible at 5 000 spots owing to the reduced film thickness.

Zincrometal K II was initially produced using one-side Zn-Ni plated steel. To enhance cosmetic corrosion resistance, the both sides of the base steel were plated with a Zn-Ni alloy (an organic coating was applied to the unexposed side only). The reason why the Zn-Ni alloy plated surface can be used as the exposed surface is largely the progress in phosphating and painting techniques already described in Sec. 2.3. However, it was also necessary to improve chipping resistance if the

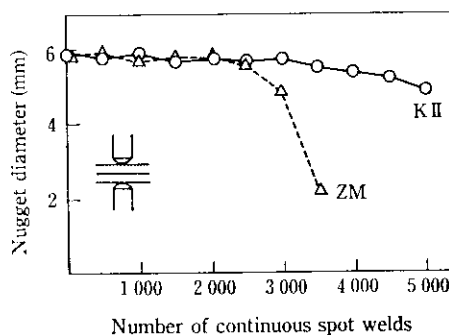


Fig. 9 Continuous spot weldability of Zincrometal K II and Zincrometal²²⁾

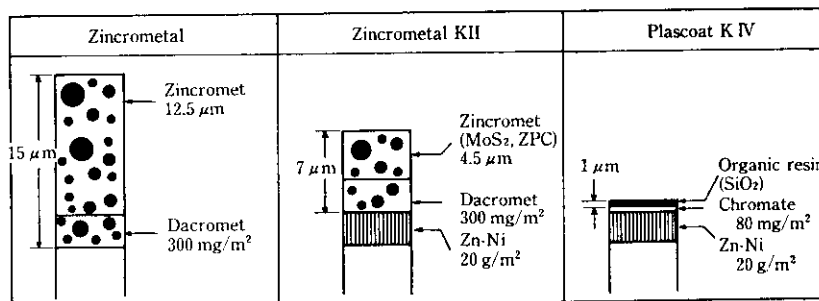
Zn-Ni plated surface was to be used in exposed panels. The Zn-Ni alloy layer is several times as hard as the zinc layer⁵⁾, and the results of a chipping test after the application of three coats revealed that the coated layer peeled off from the base steel and that the flaked area was by far larger than with cold-rolled steel sheets²³⁾. Good results were obtained by reducing the nickel content of the film to about 10%, but it was found that surface friction²⁴⁾ during press forming and phosphatability²⁵⁾ worsen because a decrease in the nickel content results in a phase containing the η phase. Therefore, the plating method was improved so that good chipping resistance was obtained even with a nickel content of 13%, making it possible to use Zn-Ni alloy platings in exposed panels.

3.3 Thin Organic Composite Coated Steel Sheets

The production of organic composite coated steel sheets requires a paint baking temperature of 270°C; the bake-hardenable steel used in automotive outer panels therefore could not be used as the base steel of organic composite coated steel sheets. To give bake hardenability to steel in the automaker's painting process after press forming, it is necessary to cure the organic film quickly at a baking temperature of 150°C or lower. To this end, Kawasaki Steel developed a thin organic composite coated steel sheet (PLASCOAT K IV) which permits low-temperature baking.²⁶⁾

The transition of the film system of prepainted steel sheets is shown schematically in Fig. 10. Plascoat K IV

Fig. 10 Schematic views of Zincrometal, Zincrometal K II and Plascoat K IV



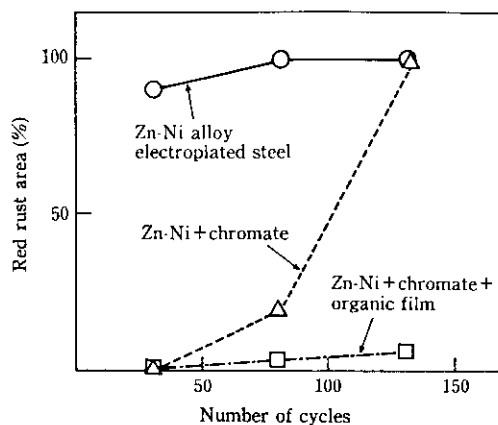


Fig. 11 Effect of chromate and organic film on corrosion resistance in cyclic corrosion test²⁶⁾

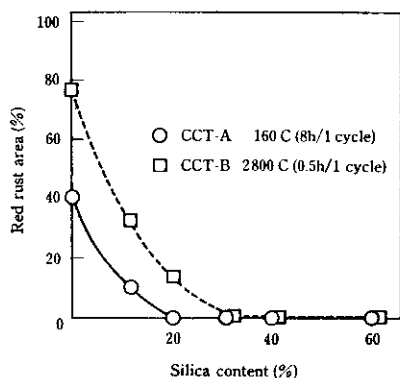


Fig. 12 Effect of silica content in organic polymer on corrosion resistance in cyclic corrosion tests²⁶⁾

is obtained by treating a Zn-Ni alloy plated steel sheet with chromate and then baking an SiO_2 -containing epoxy resin onto the chromate film at a temperature of 150°C or below. The top organic resin is a thin film of only $1\mu\text{m}$ and provides good electropaintability and weldability. Chromium, however, tends to dissolve during alkaline degreasing and phosphate treatment. This problem was solved by ensuring an appropriate $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio in the chromate and by increasing the fixed chromium ratio through the addition of a reducing agent. The corrosion resistance of precoated steel sheets is shown in Figs. 11 and 12. As shown in Fig. 11, substantial improvement in corrosion resistance is obtained only with the chromate treatment of Zn-Ni alloy plated steel sheet. On the other hand still better corrosion resistance can be obtained simply by applying a $1\mu\text{m}$ organic resin coating over the chromate film. It was also found that excellent corrosion resistance is obtained by adding 20% or more SiO_2 to the organic resin.

The excellent corrosion resistance of Plascoat K IV is attributable to the fact that passivation by the self-healing of Cr^{6+} ions in chromate and the protective action

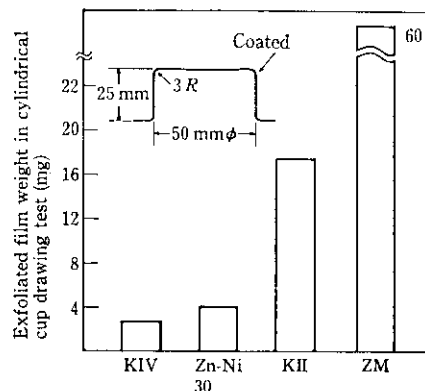


Fig. 13 Amount of exfoliated coatings of various pre-coated steel sheets after cylindrical cup drawing test

of a corrosion product (which is mainly composed of zinc hydroxide) generated in the Zn-Ni alloy plating are stably maintained by the $1\mu\text{m}$ organic resin over a long period of time. Although some researchers have concluded that the SiO_2 in the resin forms silicate,²⁷⁾ this SiO_2 in fact appears to give the resin appropriate water permeability and thereby contributes to the formation of a stable corrosion product. Exfoliated film weights after cup drawing are shown in Fig. 13. The exfoliated film weight of Zincrometal K II was reduced to 1/5 that of Zincrometal, but in Plascoat K IV, this value was improved to a level comparable with that of alloy plated steel sheet.

4 Development of Double-layered Galvannealed Steel Sheets

4.1 Galvannealed Steel Sheets

Galvannealed steel sheets are obtained by galvannealing immediately after hot-dip galvanizing to obtain a Zn-Fe alloy layer which contains about 10% Fe and is mainly composed of FeZn_7 , called the δ_1 phase. Although the corrosion potential becomes more electro-positive than zinc after galvannealing, corrosion resistance is improved since the corrosion rate is reduced, resulting in less blistering after painting and better wet adhesion. The melting point of the δ_1 phase is 670°C , which is higher than the melting point of zinc of 420°C . Therefore, electrode consumption during welding is low and spot weldability is excellent. In consideration of these points, Japanese automakers widely use galvannealed steel sheets in inner panels.

When galvannealed steel sheets are used in automotive outer panels, it is difficult to ensure the mechanical properties of the base steel as a galvannealing temperature above 500°C is required. In addition, powdering of the coated layer frequently occurs during press forming.

The use of ultra-low carbon steel as the base material made it possible to produce the deep drawable and high-strength galvanized steel sheets. Powdering property depends on the coating weight, and coating weights as light as 30 g/m² offer an adequate solution. In view of this, Kawasaki Steel developed a differentially-coated galvanized steel sheet, the outer side of which has a 30 g/m² galvanized coating and the inner side of which has a hot-dip galvanized coating of about 100 g/m² (this product is called "1 & 1/2"). Differential coating weights of 30 g/100 g are obtained by gas wiping, and the side with the lighter coating weight is galvanized. Pure zinc remains on the side with the heavier coating weight, and powdering does not occur. This galvanized product is used in automotive outer panels by American automakers.²⁸⁾

4.2 Double-layered Galvanized Steel Sheets

It was found that the problem called powdering in galvanized steel sheets is actually peeling of the coated layer from the interface between the δ phase and the Γ phase (Fe₃Zn₇) formed at the interface with the substrate steel. **Figure 14** shows the relationship between the thickness of the Γ phase and the amount of peeled zinc after a bending test of a galvanized steel sheet with a coating weight of 60 g/m². The thicker the Γ phase, the larger the amount of peeled zinc becomes. For actual pressing, the allowable maximum of peeled zinc is considered to be 2 000 cps, requiring that the thickness of the Γ phase be limited to 0.4 μ m or less. By controlling the aluminium content in the molten zinc to 0.10% or more and the iron content of the alloy layer to 12% or less, as shown in **Fig. 15**, the formation of the Γ phase is suppressed and a galvanized steel sheet excellent in powdering resistance can be produced.²⁹⁾

To use galvanized steel sheets in exposed panels, it is necessary to solve the problem of cratering during cathodic electropainting. Although cratering resistance depends on electropainting conditions, to improve the cratering resistance of the steel sheets, Kawasaki Steel applied the Fe-P plating described in Sec. 2.3 to galvanized steel sheets³⁰⁾ and developed double-layered gal-

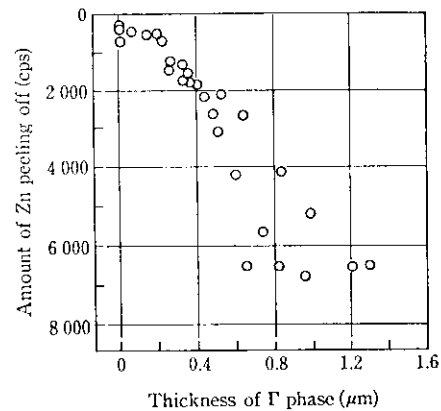


Fig. 14 Influence of thickness of Γ phase on powdering property²⁹⁾

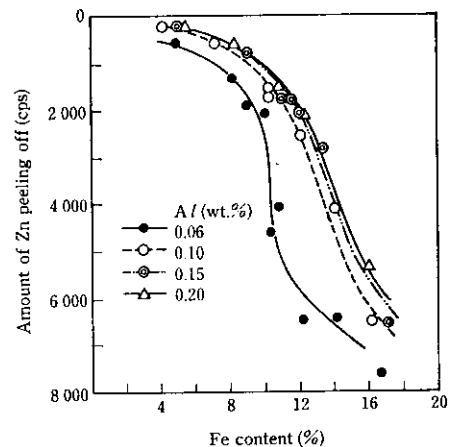


Fig. 15 Influence of Al content in Zn bath and Fe content in the coatings on powdering property²⁹⁾

vanized steel sheets with an Fe-P upper coating. In galvanized steel sheets, the occurrence of craters can be prevented by Fe-P plating with a coating weight of 3 g/m² or more. As shown in **Photo 1**, phosphate crystals form a closely-packed phosphophyllite film and phosphatability is improved.

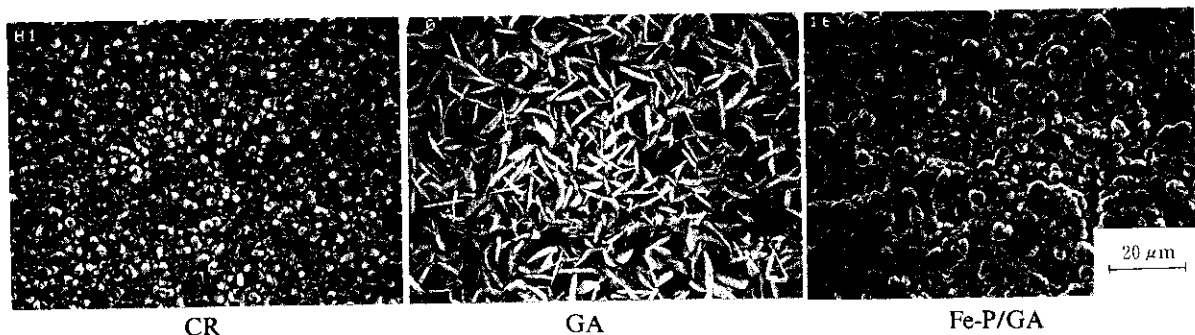


Photo 1 Scanning electron micrographs of phosphate coatings of formed on double layered hot dip galvanized steel

Galvannealed steel sheets are advantageous in terms of cost. To achieve severe rust-preventive targets of ten years for perforation corrosion and five years for cosmetic corrosion, galvannealed steel sheets, along with thin organic composite coated steel sheets, are now being used in increasing quantities.

5 Development of Dispersed Zn-plated Steel Sheet

5.1 Dispersed Zn-Co-Cr-Al₂O₃ Electroplated Steel Sheet

The recent progress in galvanized, prepainted, and galvannealed steel sheets has so far been described. These products are all produced commercially. Kawasaki Steel has also developed an ultrafine alumina dispersed Zn-Co-Cr-Al₂O₃ electroplated steel sheet (**RIVER BONA ZINC**) as a next-generation corrosion-resistant precoated steel³¹⁾, and is conducting trial manufacture and tests on an actual line.

The alloying elements in the dispersed Zn-Co-Cr-Al₂O₃ electroplated steel sheet are each included in contents of about 1%. Because a high content of alloying elements, such as that in Zn-Ni and Zn-Fe alloy plated steel sheets, results in a hard coated layer and poor adhesion, efforts were made to ensure excellent chipping resistance and wet adhesion as well as outstanding corrosion resistance in this new-generation steel by minimizing the contents of alloying elements.

The corrosion resistance of various precoated steel sheets is shown in Fig. 16. Although the Zn-Ni alloy plated steel sheet has excellent corrosion resistance in an unpainted condition, its corrosion resistance at scribed portions with 20- μ m electropainting is not good. The Zn-Fe alloy plated steel sheet has excellent corrosion resistance with painting, but its corrosion resistance

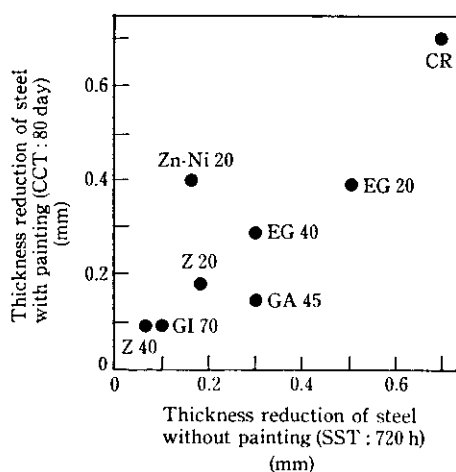


Fig. 16 Perforation corrosion resistances of pre-coated steel sheets with and without painting³¹⁾

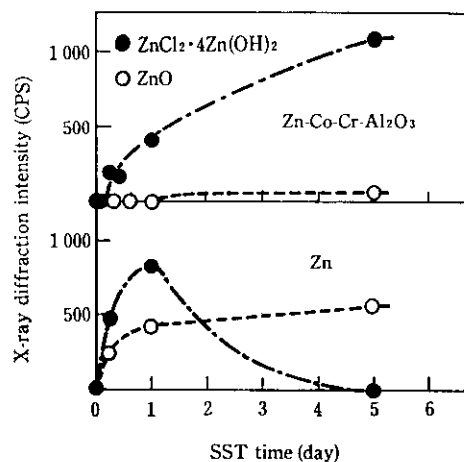


Fig. 17 Change of corrosion products on the Zn-Co-Cr-Al₂O₃ dispersed coating and electrogalvanized steel³²⁾

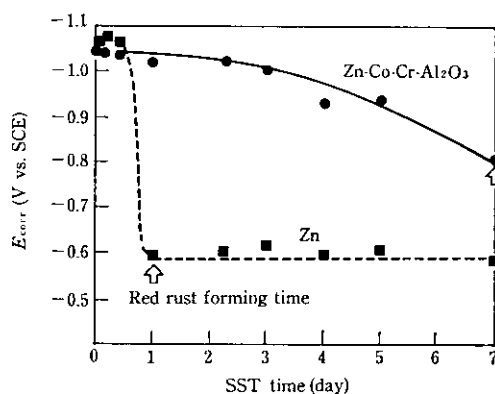


Fig. 18 Change of corrosion potential in 5% NaCl solution after salt spray test (coating weight: 20 g/m²)

without paint is not good. The dispersed Zn-Co-Cr-Al₂O₃ plated steel sheet (denoted by Z in the figure) shows excellent corrosion resistance with and without paint. The balanced corrosion resistance of this steel sheet may be explained by the fact that, as is apparent from Fig. 17, the corrosion product ZnCl₂·4Zn(OH)₂ is formed in the initial stage of corrosion and continues to exist stably for a long period of time. Cobalt contributes to the formation of ZnCl₂·4Zn(OH)₂, and high corrosion resistance is obtained by the combined effect of passivation by chromium and the stabilizing effect of Al₂O₃ on the corrosion product.³²⁾ Changes in corrosion potential with time are shown in Fig. 18. Sacrificial protection is maintained over a long period because of the low contents of alloying elements. Further, the chromium in the coating improves wet adhesion and Al₂O₃ contributes to the adhesion to the paint, thus improving corrosion resistance with painting and chipping resist-

ance.³³⁾ This product is expected to find wide use in automotive bodies in the near future.

6 Conclusions

This paper has described recent progress in precoated steel sheets for automotive use, specifically the change from the one-side galvanized sheets used mainly to provide protection against perforation corrosion to both-side galvanized steel sheets, in which cosmetic corrosion is also an important consideration. The paper has also described more recent developments in zinc-alloy electroplated steel sheets, organic composite coated steel sheets, and galvanized steel sheets.

- (1) In the field of alloy electroplated steel sheets, Kawasaki Steel developed Zn-Ni and Zn-Fe alloy electroplated steel sheets, which provide high corrosion resistance at lighter coating weights, and established manufacturing techniques using a chloride bath and soluble anodes.
- (2) For use in exposed panels, double-layered alloy plated steel sheets with an Fe-P upper layer over the alloy coated layer were developed. This product has the same phosphatability, cratering resistance, and paint adhesion as cold-rolled steel sheets.
- (3) Thin organic composite coated steel sheets were developed, featuring an organic resin film with a thickness of only about 1 μm baked at low temperature onto a Zn-Ni alloy plated steel sheet.
- (4) Double-layered galvanized steel sheets were developed, in which powdering resistance is improved by controlling alloying and excellent paintability is ensured by applying an Fe-P plating as the upper layer.
- (5) The company has also developed to the trial manufacture stage ultrafine alumina dispersed Zn-Co-Cr- Al_2O_3 electroplated steel sheets which are expected to find use as a next-generation corrosion-resistant precoated steel.

With the levels of requirements for the corrosion protection in auto bodies becoming increasingly high, the trend in precoated steel sheets is toward the use of a greater variety of alloying elements in smaller quantities, multilayering and the use of composites. Kawasaki Steel will continue to pursue a policy of developing high value-added products with easy-to-use performance which offer unique features to meet the diverse needs of customers.

References

- 1) M. Gotoh, S. Harada, and N. Ohashi: SAE Tech. Paper, 810142, Detroit (USA), (1981)
- 2) S. Kobayashi, H. Koumura, T. Ichida, T. Irie, and K. Akiyoshi, S. Azuma: *Kawasaki Steel Technical Report*, No. 12 (1985), 65
- 3) K. Sato, K. Yamato, and K. Iozumi: *Trans. ISIJ*, 23(1983),

946

- 4) A. Komoda, Y. Hirooka, K. Miyaji, T. Yoshihara, A. Matsuda, H. Yasunaga, and H. Kimura: *Kawasaki Steel Giho*, 15(1983)1, 1
- 5) K. Yamato, T. Honjo, T. Ichida, H. Ishitobi, and M. Kawai: *Kawasaki Steel Technical Report*, No. 12 (1985), 75
- 6) T. Irie, K. Kyono, H. Kimura, T. Honjo, K. Yamato, T. Yoshihara, and A. Matsuda: The AES Fourth Continuous Strip Plating Symposium Chicago (USA), (1984)
- 7) A. Shibuya, T. Kurimoto, K. Korekawa, and K. Noji: *Tetsu-to-Hagane*, 66(1980)7, 771
- 8) J. Oka, H. Asano, M. Takasugi, and K. Yamamoto: *Tetsu-to-Hagane*, 68(1982)3, A57
- 9) A. Brenner: "Electrodeposition of Alloys", Vol. 1 and 2, [Academic press, New York and London]
- 10) A. Komoda, A. Matsuda, T. Yoshihara, and h. Kimura: The AES Fourth Continuous Strip Plating Symposium, Chicago (USA), (1984)
- 11) T. Sato: *Toso Kogaku (Coating Technology)*, 20(1985)8, 106
- 12) S. Maeda, T. Asai, and H. Okada: *Boshoku Gijutsu (Corrosion Eng...ering)*, 31(1982)4, 268
- 13) T. Honjo, K. Kyono, K. Yamato, T. Ichida, and T. Irie: *Tetsu-to-Hagane*, 72(1986)8, 976
- 14) T. Saito, K. Wake, J. Oka, and M. Kitayama: *Seitetsu Kenkyu*, 315(1984), 6
- 15) T. Kojima, M. Okabe, and H. Okita: *Boshoku Gijutsu (Corrosion Engineering)*, 30(1981)10, 580
- 16) K. Yoshioka, and Y. Yoshida: *Tetsu-to-Hagane*, 69(1983)13, 121
- 17) T. Tanimura: *Jitsumu Hyomen Gijutsu (Metal Finishing Practice)*, 31(1984)12, 512
- 18) F. M. Loop: SAE Tech. Paper, 831813, Detroit (USA), (1983)
- 19) K. Furukawa, K. Tsunoyama, M. Imanaka, A. Kishida, K. Yamada, and H. Tsunekawa: *Kawasaki Steel Giho*, 20(1988)3, 203
- 20) T. Yamamoto and T. Nishikawa: *Bosei Kanri (Rust Prevention & Control)*, 18(1074)10, 31
- 21) T. Ogawa, N. Nakamura, S. Akamatsu, K. Iozumi, M. Nakamori, and S. Shijima: *Kawasaki Steel Giho*, 10(1978)1, 121
- 22) S. Tsugawa, T. Mohri, H. Hosoda, S. Kobayashi, T. Ichida: *Kawasaki Steel Technical Report*, No. 12 (1985) 94
- 23) K. Oishi, T. Nonaka, T. Kurimoto, and Y. Hobo: *Current Advances in Materials and Processes*, 1(1988)2, 704
- 24) Y. Tobiya, K. Kyono, A. Yasuda, and K. Yamato: *Current Advances in Materials and Processes*, 1(1988)2, 703
- 25) T. Kato, A. Yasuda and K. Yamato: *Current Advances in Materials and Processes*, 1(1988)5, 1638
- 26) T. Mohri, S. Tsugawa, S. Kobayashi, T. Ichida, and M. Kurosawa: SAE Tech. Paper 862030, Detroit (USA), (1986)
- 27) T. Yamashita, R. Enatsu, T. Adaniya, and T. Hara: *Tetsu-to-Hagane*, 72(1986)8, 1038
- 28) C. Belleau and D. K. Kelley: SEA Tech. paper 840284, Detroit (USA), (1984)
- 29) A. Yasuda, H. Koumura, K. Yamato, K. Onizawa, and H. Ota: Proc. World Material Congress, ASM International, Chicago (USA), (1988), 45
- 30) S. Kurokawa, K. Yamato, T. Ichida, Y. Sosiki, M. Numata, and S. Fukui: *Tetsu-to-Hagane*, 72(1986)13, S1331
- 31) S. Umino, K. Yamato, H. Kimura, and T. Ichida: *Tetsu-to-Hagane*, 73(1987)5, S424
- 32) K. Yamato, S. Umino, A. Yasuda, and T. Ichida: *Hyomen Gijutsu (The Journal of the Surface Finishing Soc. of Japan)*, 40(1989)1, 162
- 33) T. Komori, S. Umino, T. Kato, A. Yasuda, and K. Yamato: *Current Advances in Materials and Processes*, 1(1988)5, 1639