KAWASAKI STEEL TECHNICAL REPORT
No.41 (October 1999)
Advances in Iron and Steel Technologies,
Commemorating the 30th Anniversary of
Technical Research Laboratories

Recent Activities in Research of Coating

Kazuo Mochizuki

Synopsis :
Intensive research and development were conducted on coating technologies such as hot-dip galvanizing, electrogalvanizing and organic resin coating, for the purpose of extending the duration of corrosion resistance and addition of special functions. The increase of mass production of galvanized steel sheets is attributed to the application of galvannealed steel sheets and organic composite coated steel sheets to automotive panels. An outstanding development has been observed in coated steel sheets having not only corrosion resistance but also special functions such as lubricating property and anti-finger print property for home appliances and office equipment. PET film laminated steel sheet has been developed as the material for beverage cans to make it possible to harmonize the global environment and enhance production efficiency. Heavy duty organic coating has been applied to steel products for construction to assure long duration of resistance to corrosion.

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1 Technical Trends in Coating Field

1.1 Galvanized Steel Sheets for Automotive Applications

Galvannealed steel sheets and organic composite coated steel sheets, which are produced by applying a chromate treatment film and organic resin coating containing SiO_2 to a substrate of Zn-Ni coated steel, were developed to provide long term corrosion resistance in automotive bodies.

Galvannealed steel sheets with heavy coating weights of 45–60 g/m^2 can be produced efficiently. In parts which require phosphatability and electropaintability of the outer surface of the automotive body or press formability (sliding property), sheets with an Fe-P or Fe-Zn coating as the top layer were used. Because it is desirable to form a coating consisting mainly of the δ_1 phase with little Γ and ξ phase in the alloy structure of the galvannealed steel sheet, the chemical composition of the steel, concentration of aluminum in the bath, and heat pattern in the galvannealing furnace were optimized. As a low-cost technology for improving the sliding property which offers an alternative to applying a top coating layer, a borax treatment (sodium borate treatment) was developed.

Organic composite steel sheets are manufactured by applying an SiO_2 added organic resin film with a thickness of approximately 1 μm to a lightly coated Zn-Ni galvanized steel sheet with a coating weight of 20–30 g/m^2 after chromate treatment, and provide excellent corrosion resistance in the unpainted condition. The results of a detailed analysis of the corrosion suppressing effect of the thin resin film revealed that it is possible to increase corrosion resistance by controlling the hydrophilic property of the resin, and consequently, this has become an important index for resin design. Because steel sheets with a thin organic coating film are effective for improving cosmetic corrosion resistance and chipping resistance, two-side organic coated steel sheets for automotive outer panels were developed. When an organic coating is applied to an outer surface, it is necessary to control the properties of the resin in order to maintain a good appearance after electropainting. For this reason an improved resin which is different from that used on the inner surface was developed.

Moreover, it also appears that there is increasing demand for materials which are compatible with the environment. Therefore, an organic coated steel sheet with a galvannealed steel substrate for use in gasoline tanks was developed as a new product that responds to the demand for reduced use of Pb, which is a hazardous substance. This steel sheet has an epoxy resin coating

* Originally published in *Kawasaki Steel Giho*, **31**(1999)1, 34-40

with excellent resistance to gasoline on the inner side and a lubricating resin film with excellent press formability on the outer side.

In the field of rust-proof steel sheets for automotive bodies, there has been progress in the changeover to galvannealed steel sheets in Japan. In other countries, heavily coated electrogalvanized sheets and non-alloy hot-dip Zn galvanized sheets are the main types used, but a trend toward to further adoption of common materials is considered likely in the future.

1.2 Galvanized Steel Sheets for Home Appliances and Office Equipment

Flon solvents had been used in large quantities to clean processed parts manufactured from steel sheets, but restrictions were placed on the use of flons as ozone layer destroying substances. Self-lubricating steel sheets, which have a newly developed lubricant in the organic coating film, make it possible to perform deep drawing without using press oil, and the cleaning process can therefore be omitted. However, because these self-lubricating steel sheets have an organic film approximately 1 μm in thickness, their surface resistance is high, and their grounding and electromagnetic shielding properties after parts are assembled cannot be called adequate. For this reason, conductive self-lubricating steel sheets with low surface resistance were developed by applying a surface film that consists of a chromate film and lubricant.

Reactive type or dry-in-place type chromate treated steel sheets with an electrogalvanized or hot-dip galvanized substrate are used in large amounts. As a representative product which employs dry-in-place chromate, inorganic anti-fingerprint galvanized steel sheets, which possess high corrosion resistance, fingerprint resistance, and electrical conductivity, were developed.

Blackened galvanized steel sheets are sheets which are blackened by applying an electrolytic treatment to the surface of a Zn-Ni coated substrate, and are used in parts which must suppress light reflection, such as those in the interior of copying machines.

Thus, chromate treatment is extremely effective in suppressing the corrosion of zinc and makes possible a variety of functional products. Recently, a chrome-free conversion treatment technology has been desired, and research and development are progressing in this area.

1.3 Steel Sheets for Containers

PET laminated 2-piece and 3-piece cans have changed steel sheet laminating technologies, canmaking technology, and painting and printing methods. An innovative type of 2-piece can which is manufactured by the stretch draw and ironing process uses laminated steel sheets produced by heat sealing a PET film to TFS (tin free steel). As distinctive features, these cans have the good flavor property of PET film and employ an outstanding canmaking process which consumes little energy and produces no waste during canmaking. A laminating line was constructed to realize continuous operation in TFS production (Cr plating) and application of the film, and production is being carried out efficiently.

For 3-piece cans, a PET film with a design applied by printing is laminated on the steel sheet using an adhesive. Because conventional seam welding is used as the canmaking method, lightly tin coated steel sheets for welded cans "Riverwelt", which have excellent weldability and adhesion with films, are used as the substrate steel sheet.

2 Organic Composite Coated Steel Sheet for Automobiles "Plascoat KV"

2.1 Film Structure

Plascoat KV is a steel sheet to which a chromate layer with a Cr coating weight of 80 mg/m^2 and an organic resin layer approximately 1 μm in thickness and containing 40% SiO_2 are applied to one side of a two-side coated Zn-Ni galvanized sheet generally having a coating weight of 20–30 g/m^2. The baking temperature of the resin layer is a peak metal temperature of approximately 150°C. When this product is applied to the outer panels of the automotive body, the thickness of the chromate layer and resin are reduced to approximately 1/2.

2.2 Properties of Film and Unpainted Corrosion Resistance

The properties of the resin film and corrosion resistance of organic composite coated steel sheets were investigated. Samples were prepared by coating two types of Zn-Ni galvanized steel sheets (EZN), i.e. with and without a chromate layer, with a hydrophobic resin (A) or hydrophilic resin (B). The samples were subjected to 200 cycles of a composite corrosion cycle test (CCT), and the red rust area ratio was measured. The results are shown in **Fig. 1**. A remarkable improvement in corrosion resistance was observed when the hydrophilic resin was applied, regardless of the presence or absence of the chromate layer.[1] Next, the two types of resin mentioned above were applied to Zn-Ni coated steel sheets, and 21 cycles of the same CCT were performed to cause corrosion, and the corrosion products which formed on the coated surface were analyzed by X-ray diffraction. With the hydrophobic resin, which had low corrosion resistance, the presence of basic zinc hydroxide and zinc oxide was found. In contrast, with the hydrophilic resin, only basic zinc hydroxide was detected.[1] It was assumed that the corrosion resistance of the hydrophobic resin was low because zinc oxide has electrical conductivity, whereas the excellent corrosion resistance of the hydrophilic resin was attributable to the formation of desirable corrosion products.

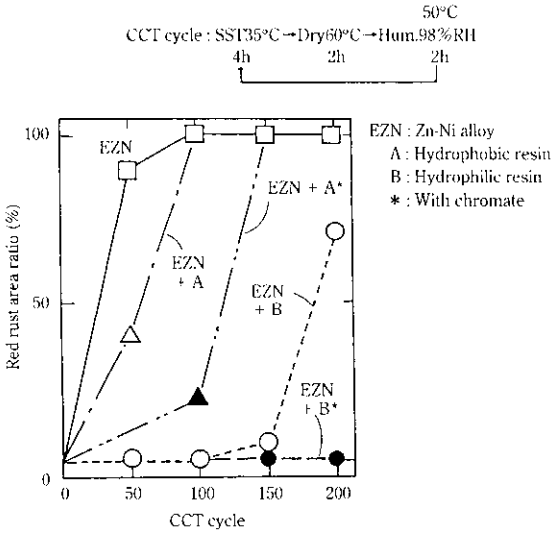

Fig. 1 Effects of resin type and chromate on the corrosion resistance of the organic composite coated steel sheet

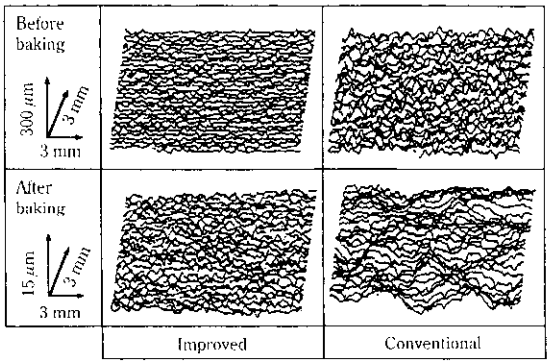

Fig. 2 Three-dimentional surface roughness of ED-painted PLASCOAT KV

2.3 Chipping Resistance and Clarity after Painting

Because the hardness of the Zn-Ni coating layer is high, peeling tends to occur easily at the interface between the coating layer and the steel sheet when small stones fly up while the car is travelling and strike the car body. Consequently, cosmetic corrosion originating at such points was a problem. In a chipping test in which three paint coats were applied to the resin surface of an organic composite coated steel sheets, it was found that the paint peeling area decreased remarkably and low temperature chipping resistance improved. Because the galvanized layer remained even in parts where only slight exfoliation damage of the paint film had occurred, corrosion originating at these points was markedly reduced.

On the outer surface of car bodies, a good paint finish is required. Waves occurred when the electro deposited paint film was affected by the thin organic film, and there were cases in which the clarity of the paint surface after three coats deteriorated. Because electro deposited paint films use water as the solvent, the resin precipitates and coats the steel surface as a result of the increase in pH which occurs due to hydrogen generation when the electro deposition current is applied. Before baking, the sheet has wave components due to traces of hydrogen generation and other factors, but when baking is performed, the paint film flows and becomes smooth before hardening. However, waves with a long period are not smoothed even by the flow during baking, and have a detrimental effect on clarity. The results of an investigation showed that wetting between the organic film at the top layer of the organic coated sheet and water, which is the solvent for electro deposited paint, has an effect on waves with a long period. **Figure 2** shows the results of a measurement of the 3-dimensional surface roughness when two types of organic coating resins with different wettability were applied and electro deposition painting was performed. It was clear that a resin with improved wettability, as mentioned above, reduces long period wave components of 0.4 mm and longer, resulting in excellent clarity in the painted surface.

3 Galvannealed Steel Sheets for Automotive Applications

3.1 Structure and Mechanical Properties of Steel

The CGL is a process in which the annealing process, coating and alloying processes, at 450–550°C, are performed continuosly. Using ultra-low carbon steel base material with stabilized C and N, excellent material properties could be obtained without additional treatment. Compound addition of Ti-Nb to ultra-low carbon steel base material improves the r value, El, YS, and other properties of Nb bearing steel. However, because white streaks occur when the Ti content exceeds 0.03%, a steel sheet base material with excellent mechanical properties suitable for the CGL was developed by minimizing the C and N contents of the steel and holding the Ti content below this value.[2)]

3.2 Press Formability

3.2.1 Sliding property

In press formability, in addition to the mechanical properties of the steel sheet, the sliding property, which originates in the phase structure of the coating layer, is also important. If the coefficient of friction is high, the sliding length of the sheet during forming will be insufficient, and cracking may occur. **Figure 3** shows the change in the coefficient of friction, which was measured in the non-oil coated condition by the bead-draw

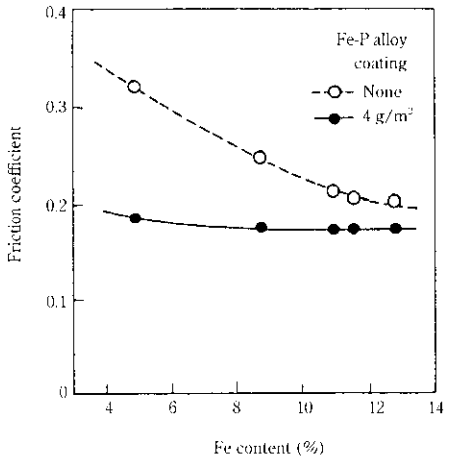

Fig. 3 Change in friction resistance of galvannealed steel sheet according to an increase in Fe content of coating

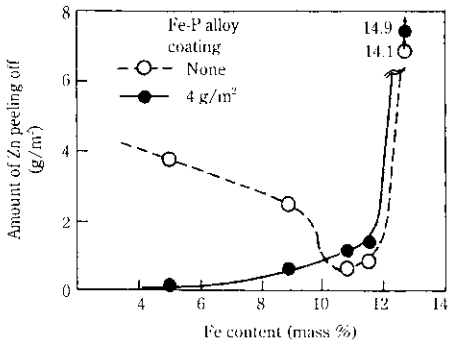

Fig. 4 Influence of Fe content on amount of coating peeling off during passing through bead model

method using a round-shaped bead, for cases in which an Fe-P coating was or was not applied to galvannealed steel sheets with differing Fe contents. When the Fe-P coating was applied, the sheets showed a constant, low coefficient of friction which was independent of the Fe content. In contrast, the coefficient of friction of the uncoated sheets decreased as the Fe content increased, but the value of the coefficient of friction was higher in all cases with coating than without coating.[2] With an Fe content of 8%, the existence of the ξ phase, which shows an inferior electric potential, was observed. However, with an Fe content of 11%, virtually only the δ_1 phase was present.[2] The reason why the sliding property of galvannealed steel sheets changes depending on the Fe content is because the phase structure of the intermetallic compounds which comprise the coating layer changes. Specifically, the ξ phase appears when the Fe content is low. Because the hardness of this phase is low, sticking between the sheet and die occurs more easily and the coefficient of friction increases as the ratio of this phase increases.

3.2.2 Coating peeling property

Peeling of galvannealed coatings is of two types, depending on the Fe content. One is the phenomenon known as flaking, which occurs when the Fe content is low and the ratio of the ξ phase is high. In this case, the coefficient of friction increases, and the coating is peeled off by the die. On the other hand, when the Fe content is high, the coating is exfoliated in a powdery form. This phenomenon, known as powdering, is caused by the Γ phase which forms between the coating phase and the steel sheet. When the amount of peeling is measured by performing a bead-draw test on galvannealed steel sheets with and without an Fe-P coating in the same manner as in the previous section, large exfoliation by flaking occurs in sheets without Fe-P coating when the Fe content is low, as shown in **Fig. 4**.[2] In contrast to this, when the Fe content is high, the amount of powdering increases markedly, independently of the presence or absence of a top layer coating. This is caused by the difference in the mechanisms of peeling by flaking and powdering, as described above.

Based on these results, a technology for controlling alloying to produce a single δ_1 phase, together with controlling the Fe content to 8–11%, is extremely important.

3.3 Spot Weldability

With hot dip galvanized steel sheets using ultra low carbon steel sheets with a compound addition of Ti-Nb as the substrate, the number of continuous welding spots is lower than when low carbon steel sheets are used as the substrate. With ultra low carbon sheets, the sheet becomes markedly softer during welding, and the thickness of the sheet being welded is reduced by the pressure applied by the electrode. As a result, the temperature increase at the tip of the electrode becomes excessive, accelerating electrode wear. The reason for this was thought to be softening of the sheet due to grain growth in the heat affected zone. Therefore, the material was improved by adding 0.000 5% B to the steel to suppress growth, resulting in an increase in the number of welding spots.

4 Self-lubricating Steel Sheets "River Zinc FS and FE"

Zinc galvanized steel sheets which are to be used in the internal parts of household electrical appliances and office equipment are frequently applied without painting, by performing a rust-preventive treatment such as chromate treament. In the forming process for sheets, the sheet is coated with a lubricating oil, following by cleaning. However, there were problems with these sheets, such as deterioration of the working environment by splashed lubricating oil and difficulty in meeting the

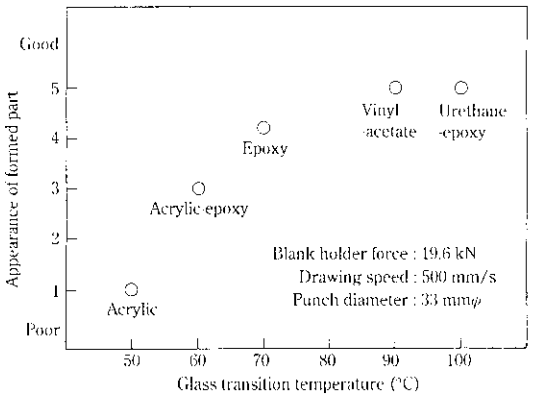

Fig. 5 Effect of glass transition temperature T_g of resin on appearance of formed part

Table 1 Comparison of performance of self-lubricating steel

Property	RIVER ZINC FE	RIVER ZINC FS	RIVER ZINC FX
Surface electric resistance (Ω)	< 0.5	1~100	0.5
Number of electrode chip life for spot welding	> 3 000	150	> 3 000
Coeffiicient of friction by drawing test	0.15~0.25	0.10	0.35~0.45
Press formability of LDR by cup drawing test	2.09	2.33	< 1.8
Corrosion resistance by salt spray test (h)	> 100	> 200	> 100

environmental regulations applied to the organic solvents used in cleaning. Self-lubricating steel sheets are produced by performing chromate treatment and then applying an organic resin which contains a lubricant to a galvanized steel substrate. These sheets have excellent formability without oil coating, and thus not only solve the above-mentioned problems at a single stroke, but also provide improved corrosion resistance and an anti-fingerprint property. This section describes the structure of the film and the quality performance of these products.

4.1 Film Structure and Quality Performance of River Zinc FS

The influence on powdering of the resin and lubricant which comprise the organic film, the coating weight, and the baking temperature was investigated. A high speed cylindrical drawing test was conducted using five types of resin applied to galvanized steel sheets. Polyolefin wax was added to the resin at a ratio of 0.1 part wax to 1 part resin. No differences in the limit blank holding force were observed. However, as shown in **Fig. 5**, the highest powdering resistance was shown by the vinyl-acetate and urethane-epoxy resins, which have high glass transition temperatures of 90–100°C.[3] The vinyl-acetate resin was selected as the base resin based on the favorable results obtained in a separate test of corrosion resistance.

The resin coating weight was set in the range of 0.6 to 1.4 g/m^2, which are the lower limit value for obtaining an adequate sliding property and the upper limit value for avoiding powdering. Baking temperatures of 120–180°C gave satisfactory results. This range was set based on the lower limit value for adequate thermosetting, and an upper limit value which is near the thermal decomposition temperature and at which the cohesive force and adhesive force would be reduced.

Because River Zinc FS is excellent not only in press formability, but also in the anti-fingerprint property and corrosion resistance, increasing demand is expected.

4.2 Film Structure and Quality Performance of River Zinc FE

With expanded application of self-lubricating steel sheets coated with organic resin, there has been increasing demand for self-lubricating sheets which provide excellent surface conductivity, including a grounding property and electromagnetic shielding property, and weldability. Because it is not desirable to increase conductivity so long as an organic resin is used as the coating film, studies were conducted from various points of view. As a result, it was possible to obtain a conductivity of 0.5 Ω or less with River Zinc FE, in contrast to the conductivity of 1–100 Ω of the conventional River Zinc FS, by forming a dry-in-place chromate layer containing dispersed polyolefin wax with a particle size of 0.2 μm.[4] **Table 1** shows a comparison of these self-lubricating steel sheets and inorganic anti-fingerprint galvanized steel sheets.

5 High Performance Treated Steel Sheets

The organic anti-fingerprint steel sheet, "River Zinc F," with a thin organic film as its surface, possesses high corrosion resistance and an excellent anti-fingerprint property, and is widely used a material for interiors. In addition to these properties, the high corrosion resistance, inorganic anti-fingerprint galvanized steel sheet, "River Zinc FX," was developed in order to improve conductivity and resistance to solvents. River Zinc FX is produced by coating and baking a treatment solution consisting of silica and chromate. The formed film is excellent in uniformity of the color tone, with white as the basic tone. This steel sheet has excellent performance in terms of appearance, showning very little soiling due to fingerprints and oil in processing and assembly work.[5]

The blackened galvanized steel sheet, "River Zinc Black," is a steel sheet with a Zn-Ni layer, blackened

layer, conversion film layer, and resin layer on a steel sheet. This sheet has L values of 12–15, and a low gloss black appearance with a glossiness value of 20–25. Its black appearance is maintained even in parts which are processed by drawing, and corrosion resistance is high, at 200 h or more until 5% white rust in the SST corrosion test. This product has excellent solvent resistance and surface properties such as silk printability, etc., and spot weldability exceeding 2 000 continuous spots. Based on these properties, it is widely used in the interior components of office equipment, audio equipment, and household electrical appliances.

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