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Properties of Iron-Zinc Alloy-Electroplated Galvannealed Steel Sheet

Tatsuya Kanamaru*1 Jun-ichi Morita*1
Motohiro Nakayama*2 Katsutoshi Arai*1
Yutaka Ogawa*3

Abstract:

A new iron-zinc alloy-electroplated galvannealed sheet was developed to meet the demand for heavily coated corrosion-resistant steel as a means of enhancing the corrosion protection of automobiles. The new sheet product has an 80% iron-zinc alloy electroplated at a coating weight of 3 g/m² on a galvannealed coating. The heavy lower layer or galvannealed coating provides corrosion resistance over a longer term, while the upper layer or iron-zinc alloy coating provides improved electrodeposited primer finish, phosphatability and press formability. The heavy-coating weight sheet can be used for both exposed body panels and hard-to-form inner panels.

1. Introduction

In winter, deicing salt and sand are spread on roadways to create an extremely corrosive environment for automobiles. The average service life of automobiles now exceeds 10 years in advanced countries. Several years ago, the big three automakers of the United States announced ten years of perforation corrosion warranty and five years of cosmetic corrosion warranty. These warranty periods are now recognized as automobile corrosion performance goals throughout the world. These goals will stand valid for the future.

The use of corrosion-resistant steel sheet is the most reliable measure for the corrosion protection of automobiles. Increasing the coating weight is most effective in assuring 10 years of perforation corrosion resistance and 5 years of cosmetic corrosion resistance. For economic reasons, conventional electroplated corrosion-resistant steel could not be increased in coating weight, and this brought galvannealed steel into spotlight. In the past, galvannealed steel with a coating weight of 45 g/m² was used mainly in inner body panels. Recently, technology was developed to manufacture galvannealed sheet products with a coating weight of 60 g/m² to meet the requirement for higher-coating weight[1]. The use of galvannealed steel in outer body panels called for an improvement in electrodeposited primer finish and phosphatability. Also some measure had to be taken against the increase of shear stress that would act on the coating layer of heavy-coating weight galvannealed steel during press forming.

The iron-zinc alloy-electroplated galvannealed steel sheet (known by the trade name acronym AS-E) has a lower galvannealed coating and a 3-g/m² upper 80% Fe-Zn alloy electroplated coating. The heavy lower coating provides longer-term corrosion protection, while the upper iron-zinc alloy coating provides better press formability, electrodeposited primer finish, and phosphatability. Described hereunder are the properties of the iron-zinc alloy-electroplated galvannealed steel in application as corrosion-resistant steel for automobiles.

2. Coating Composition

Fig. 1 shows the coating composition of the iron-zinc alloy-electroplated galvannealed steel for outer body panels. The lower layer is an approximately 10% Fe-Zn alloy coating deposited by the hot-dip process. The coating weight is 30 g/m² on the outer surface to meet the 5-year cosmetic corrosion warranty and is 60 g/m² on the inner surface to meet the 10-year perforation cor-

*1 Technical Development Bureau
*2 IN/KOTE Technology
*3 Nagoya Works

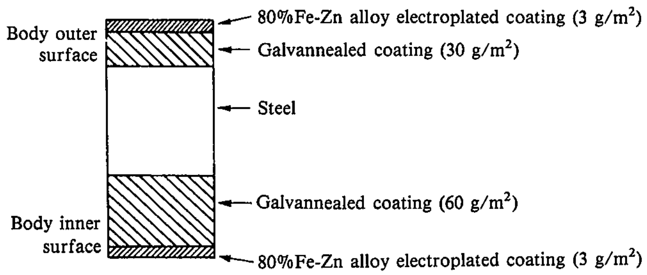

Fig. 1 Coating composition of iron-zinc alloy-electroplated galvannealed steel (for automobile body outer panels)

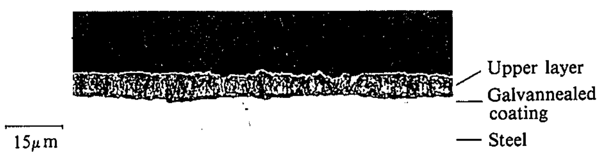

Photo 1 Cross-sectional microstructure of iron-zinc alloy-electroplated galvannealed steel

rosion warranty. For inner body panels, the coating weight of the lower layer is 60 g/m^2 on both surfaces. The upper layer is an 80% Fe-Zn alloy coating deposited to 3 g/m^2 by the electroplating process. The upper layer is particularly effective in improving paint adhesion on the outer surface and has the effect of improving lubricity during press forming on both inner and outer surfaces. The upper-layer coating weight of 3 g/m^2 was determined to allow for phosphatability and press forming lubricity as described later. Regarding the Zn-Fe composition, the 10% Fe content of the lower layer is best for underfilm corrosion resistance[2)], and the 80% Fe content of the upper layer is designed to minimize the difference of corrosion potential from the lower layer[2)] and to increase hardness.

Photo 1 shows the cross-sectional microstructure of the coating of the iron-zinc alloy-electroplated galvannealed steel. The lower galvannealed coating consists of a hexagonal δ_1 phase and has severe surface irregularities, but is covered with the upper layer to present a uniform final surface smoothness.

3. Quality

3.1 Corrosion resistance

Corrosion-resistant steel sheets for automotive use are required to resist perforation corrosion and cosmetic corrosion. Perforation corrosion resistance is specified for such automobile parts as hem flanges that cannot be properly painted and are subject to corrosion by the entry of water or oxygen in the field environment. **Fig. 2**[3)] shows the results of perforation corrosion tests on electroprimed steel sheet lap specimens. Each specimen was immersed in a 1% muddy salt solution for 1 day and left to stand in the laboratory for 6 days. This cycle was repeated for 50 weeks to simulate the corrosive environment of automobiles in the field. Corrosion resistance is known to increase with increasing coating weight. The inside of the lap is bare. During the cyclic corrosion test, an oxygen concentration cell is established and makes the inside of the lap an anode. The coating weight thus governs the duration of sacrificial protection. The iron-zinc alloy-electroplated galvannealed steel allows an increase in the coating weight of the lower layer, so that it can acquire additional perforation corrosion resistance.

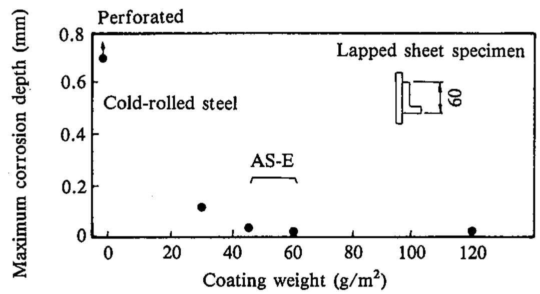

Fig. 2 Results of perforation corrosion test of lapped sheet specimens (20-μm electrodeposited primer, 50 cycles)

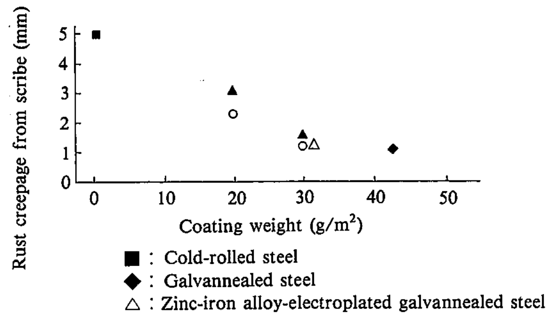

Fig. 3 Results of atmospheric exposure test in Okinawa (3-coat painted steel, 1-year exposure)

Cosmetic corrosion resistance refers to the prevention of corrosion from spreading from damages caused on body panel surfaces by gravel and other impinging objects. Three-coat painted sheet specimens were scribed and exposure tested in Okinawa. The results of the exposure test are shown in **Fig. 3**[3)]. The scribe on the cold-rolled steel bulged into a scab rust, and the paint surface around it was marked by running red rust. On the iron-zinc alloy-electroplated galvannealed steel, on the other hand, scarcely developed underfilm creepage or apparent red rust at the lower-layer coating weight of 30 g/m^2. In other words, the iron-zinc alloy-electroplated galvannealed steel proved to be fully capable of retaining the good appearance of automobile body panels.

3.2 Paintability

Concerning the paintability of corrosion-resistant steel sheet attention must be focused on good paint adhesion and attractive paint finish. Success in satisfying the former requirement heavily depends on the properties of the phosphate film. Since the phosphate film is formed through the reaction of the metal coating with the phosphating solution, the surface properties of the metal coating ultimately govern the paint adhesion of the corrosion-resistant steel. **Fig. 4**[4)] shows the relationship between the coating weight of the upper layer and the P-ratio of the phosphate film (proportion of phosphophyllite in the phosphate film). When the steel is coated with the lower layer alone, only acicular crystalline hopeite [$Zn_3(PO_4)_2 \cdot 4H_2O$] is formed. When the upper layer is coated to a weight of 2.5 g/m^2 or more, there is obtained a film mainly composed of tight granular crystals of phosphophyllite [$Zn_2Fe(PO_4)_2 \cdot 4H_2O$]. This is because the iron-rich upper layer is dissolved in the phosphating solution and precipitated as phosphophyllite. Phosphophyllite is highly effective in improving the underfilm blistering resistance of the iron-zinc alloy-electroplated galvannealed steel[5)].

One problem associated with the paint finish of zinc-coated

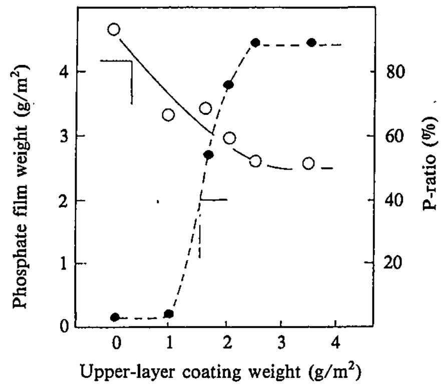

Fig. 4 Coating weight and phosphatability of upper layer

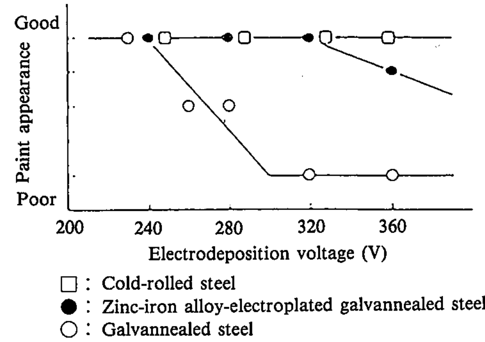

Fig. 5 Electrodeposition voltage and paint appearance

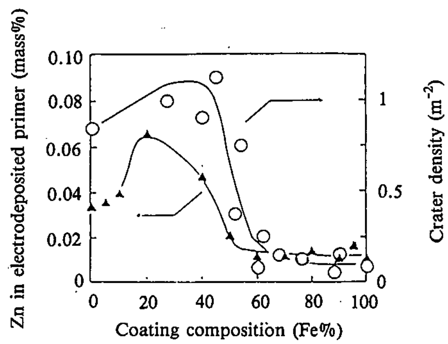

Fig. 6 Relations of iron-zinc alloy coating composition with crater density and zinc content of electrodeposited primer

steel is paint film defects, namely, craters and pinholes, occurring during the electrodeposition of the primer. The application of current during electropriming produces hydrogen gas below the precipitated primer film. The hydrogen gas closes the current path and causes spark discharge. The primer film is partly precured by the spark discharge to become craters[6,7]. The tendency to spark discharge occurrence depends on the applied voltage and the surface properties of the material concerned. The outside surface of automobile bodies is located close to electropriming tank electrodes where cratering tends to occur. As particular importance is attached to the paint appearance of outer body panels, any cratering poses a serious production problem. Preventing cratering is prerequisite to the use of corrosion-resistant steel in automobile body outer panels.

Fig. 5[3] shows the relationship between the electrodeposition voltage and the primer appearance. The iron-zinc alloy-electroplated galvannealed steel is found to have no cratering under practical electrodeposition voltages. This attests to the effectiveness of the iron-rich upper layer, as shown in **Fig. 6**[8]. The reason may be as follows. During the precipitation of the electrodeposited primer, the pH at the interface exceeds 12, where zinc is dissolved from the zinc-rich lower layer while generating hydrogen gas. The interface is thus considered to be under the condition where spark discharge occurs. In the iron-rich composition range, on the other hand, the attenuation of the cathode current by the resistance of the primer film stops the evolution of hydrogen and prevents the spark discharge. This is because the dissolution rate of the upper layer during the electrodeposition of the primer is low. **Fig. 6** includes the amount of zinc trapped during the electrodeposition of the primer. The reason why cratering is prevented by the iron-rich upper layer can be understood if this amount of entrapped zinc is considered to be proportional to the amount of hydrogen generation.

3.3 Press formability

Among the problems associated with the properties of coatings are the surface lubricity and peeling off by working. In press forming, the metal flows into the die while being subjected to large contact pressures in the die shoulder and beads. The sliding resistance developed here influences steel fracturing and wrinkle by the tension applied to the steel. The sliding resistance also produces shear stress at the interface between the coating and the steel. When the shear stress exceeds the yield strength of the coating, it cause a peeling off of the coating. When peeled coating flakes drop into the die, they cause dents in the panel being formed, resulting in a production trouble.

Galvannealed steel has iron diffused into the zinc coating to form an alloy predominantly composed of δ_1 phase ($FeZn_7$). As the coating weight increases, the difference of iron concentration between the coating surface and steel substrate increases. A low-iron ζ phase ($FeZn_{13}$) tends to form on the surface, while a high-iron Γ_1 phase (Fe_5Zn_{21}) is appreciably formed at the interface with the steel substrate. When the soft ζ phase is present on the surface of the galvannealed steel, it adheres to the die and increases the sliding resistance of the galvannealed steel during press forming. When the hard and brittle Γ_1 phase grows thickly at the interface, it fails to withstand the applied shear stress and is liable to peel.

The above-mentioned weaknesses of the heavy-coating weight galvannealed steel can be solved by applying the iron-rich upper layer. **Fig. 7**[9] shows the effect of the upper layer on the drawing load in the draw bead test. The upper-layer coating increases the surface hardness of galvannealed steel, which in turn decreases the drawing load. When the coating weight of the upper layer is 2.5 g/m^2 or more, surface lubrication characteristics are replaced by the properties of the upper layer.

Fig. 8 shows the effect of the upper-layer coating on the press formability of galvannealed steel as compared with lubricating oil in cupping test. The blankholder force range where wrinkling and cracking do not occur are the forming limit range, which depends on the r value and lubrication of the material concerned. When galvannealed steel is compared in the lubrication effect with lubricating oil at the same r value, the forming limit range expands with increasing oil viscosity. The cracking limit is high also when a solid lubricant is applied. When lubricated with a low-

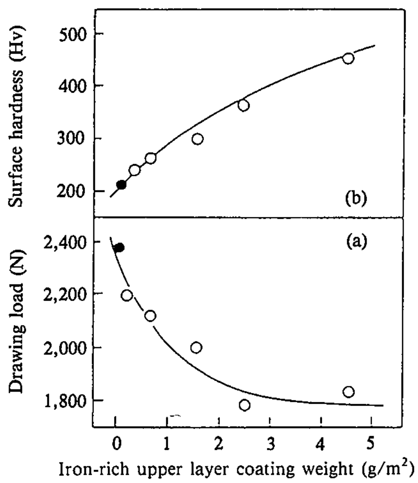

Fig. 7 Effect of upper layer in draw bead test

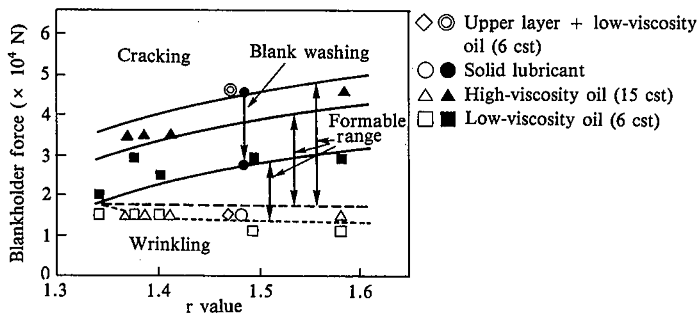

Fig. 8 Effect of upper-layer coating on formable range of galvannealed sheet steel as compared with the effect of lubricating oil (cupping test)

viscosity oil, the upper-layer coating exhibits a forming limit range equal to or better than that provided by the solid lubricant. At automobile stamping shops, body outer panels are washed on blanking lines to prevent dents from dust, dirt, and other foreign matters. The cracking limit for the solid lubricant when removed by washing with oil is shown to fall to that of the low-viscosity lubricating oil. These results indicate that the iron-zinc alloy-electroplated galvannealed steel has the best lubricity as body outer panel material to be processed through the washing line.

The effect of the upper layer on the peeling performance of the coating is shown in **Fig. 9**[9]. Various panels were passed over beads and evaluated for the resultant peeling of the coating. The upper layer was thus found to be very beneficial. The initiation point of the peeling of the coating lies in the Γ_1 phase. The shear force imposed on the coating is reduced by the lubricity of the upper layer. The upper layer improves the paintability of galvannealed steel and is favored for body outer panels, as already described. It was also proved to be applicable with advantage to hard-to-form inner panels, such as rear floor and wheel house parts.

4. Manufacturing Technology

The electroplating of an 80% iron-zinc alloy is an industrially established technology for the application of an upper layer to the iron-zinc alloy-electroplated steel[2]. With the iron-zinc alloy-electroplated galvannealed steel, however, the lower galvannealed coating constitutes a very irregular surface composed of hexagonal δ_1 phase, and is covered by an oxide film. Electroplating this surface with the upper layer calls for special considerations. Fortunately, the iron-rich upper layer electrodeposits efficiently on an uncovered zinc-rich surface, where the hydrogen overvoltage is high. As a result, the upper layer can uniformly cover complicated shapes. It is essential that the zinc and aluminum oxide films should be fully dissolved and removed from the lower layer before the electrodeposition of the upper layer.

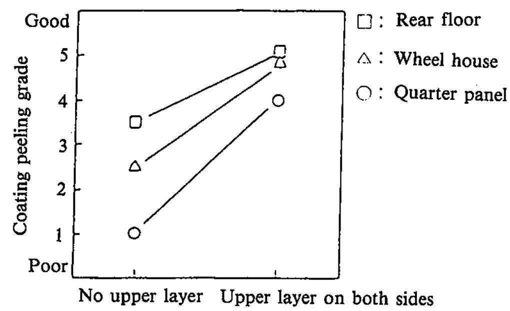

Fig. 9 Effect of upper layer on peeling of coating

Industrially, electrolytic cells are placed in the rear part of a continuous galvanizing line to produce steel sheet coated with two layers, that is, the lower galvannealed coating and the upper iron-zinc alloy electroplated coating, within one line.

5. Conclusions

The iron-zinc alloy-electroplated galvannealed steel technology is characterized by improved performance and operating ease with a unique double-layer coating structure designed in response to the demand of the times for increased anti-corrosion coating weight to enhance the corrosion protection of automobiles. Paintability and press forming lubricity are boundary issues and are common subjects of surface technology in bordering fields. Among them, the technology presented herein represents a practical solution to the above issues in the field of steel surface treatment. The iron-zinc alloy-electroplated galvannealed steel is produced in large quantities for automobile body outer panels and hard-to-form inner panels. The technology is exported today.

Acknowledgments

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