

Pb-free Coated Steel Sheets for Fuel Tanks

Masao KUROSAKI*1
Teruaki IZAKI*3
Masahiro FUDA*4
Shinichi SUZUKI*2

Kenichiro MATSUMURA*2
Jun MAKI*1
Akihiro MIYASAKA*4

Abstract

Pb-8mass%Sn coated steel sheet (which is known as terne sheet) has been widely used for automotive fuel tanks because of its well-balanced properties during tank manufacturing and durability under severe corrosion circumstances. Reduction of lead has become an urgent topic in discussions on ways to reduce the burden on the environment. Nippon Steel Corporation has developed alternative steel sheet. They are hot dip Sn-Zn alloy coated steel sheet and GI-Ni double-layered steel sheet, which has electro-galvanized Ni on hot dip Zn coatings (GI). Both of them are capable of providing: (1) good internal corrosion resistance, (2) good external corrosion resistance, (3) good solderability and resistance weldability, and (4) good press formability. They have been already adopted by many automobile producers and significantly reduced the use of lead for automobiles.

1. Introduction

A Pb-Sb-alloy-coated steel sheet (known as a terne sheet) has been used as the main material of automobile fuel tanks by virtue of its properties that satisfy the requirements for the fabrication and use in tanks in a well-balanced manner. The amount of the Pb coating for a fuel tank is 200 g or so, accounting for roughly 11% of Pb used for an automobile¹⁾. Over the last years, however, the restrictions of the use of Pb and other environmentally hazardous materials have been tightened. Specifically, under Directive 2000/53/EC, enacted in October 2000, the EU banned the use of Pb (and Hg and Cd, too) for the components of automobiles to be sold in July, 2003 and thereafter, although some components are exempt from the rule. In Japan, the Ministry of International Trade and Industry (now the Ministry of Economy, Trade and Industry) proposed, in the target recycling rate of used cars, that the use of Pb be reduced to one half that in 1996 or less by the end of 2000, and to one third or less by the end of 2005¹⁾.

To cope with the above trend of regulations, Nippon Steel Corporation has developed coated steel sheet products free of Pb for fuel tank use: a hot-dip Al-Si-alloy-coated steel sheet; a hot-dip Sn-Zn-alloy-coated steel sheet; and a GI (hot-dip zinc plating)-Ni double-layered steel sheet.

2. Pb-free Coated Steel Sheets for Fuel Tanks

The following properties are required of a steel sheet used for a fuel tank of an automobile: (1) corrosion resistance of the inner surface (resistance to gasoline), (2) corrosion resistance of the outer surface (resistance to salt damage), (3) welding & joining properties (solderability, resistance weldability), and (4) press formability. A fuel tank is one of the essential components for ensuring driving safety, and because fuel leakage resulting from corrosion can lead to serious accidents, durability against corrosion is the most important characteristic required of its material. With regard to the corrosion resistance of the inner surface, in particular, what is essential is the

*1 Yawata R&D Lab.
*2 Nagoya R&D Lab.

*3 Yawata Works
*4 Steel Research Laboratories

corrosion resistance in an environment containing formic acid and acetic acid, which form through the oxidation and degradation of olefinic hydrocarbons, the main constituents of gasoline. The saddle type fuel tank of a four-wheel-drive car, which has become popular lately, has a complicated shape, and a good press formability to permit such forming work has become one of the important properties of a material steel sheet. For these reasons, a steel sheet for an automobile fuel tank must have all the characteristics required for each of the stages from the fabrication to the final use in a well-balanced manner.

To meet these requirements, a hot-dip Sn-Zn-alloy-coated steel sheet^{2,3)}, a hot-dip Al-coated steel sheet⁴⁾, a galvanized steel sheet with organic coating films^{5,6)}, a GI (hot-dip zinc plating)-Ni double-layered steel sheet, and so forth have been developed in Japan, and they have actually been used at car manufacturers. Outside Japan, a hot-dip Al-coated steel sheet⁷⁾ has been used in Europe, and a Zn-Ni-alloy-coated steel sheet with organic coating films⁸⁾ in U.S.A.

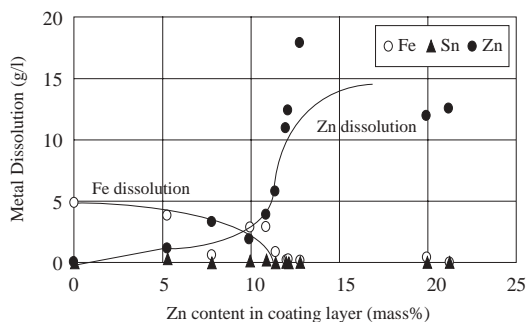
Among the above-mentioned three coated steel sheet products Nippon Steel developed, this paper describes the hot-dip Sn-Zn-alloy-coated steel sheet, which is as excellent as a terne sheet in most of the properties required for tank fabrication and better yet in corrosion resistance, and the GI-Ni double-layered steel sheet, which has properties substantially equal to those of a terne sheet in a mildly corrosive environment and can be produced at a low cost.

3. Hot-dip Sn-Zn-alloy-coated Steel Sheet

3.1 Optimum coating layer structure

The hot-dip Sn-Zn-alloy-coated steel sheet was developed at Nippon Steel's Yawata Works as an economical steel sheet product capable of being produced on an existing terne sheet production line and used without modifying the tank fabrication processes of a user. It was designed to take advantage of the ductility and corrosion resistance of Sn together with the effect of Zn as a sacrificial anode; the content of Zn in the coating layer is set at 7 to 9 mass %, less than the eutectic percentage, so that Zn disperses in fine grains. The product is outlined below.

Fig. 1 shows the relationship between the Zn content (in mass %) in the coating layer and the dissolution of metals in a solution of degraded gasoline. While the dissolution of Zn increases as its con-



Test solution: mixture of regular gasoline + degraded gasoline + 10% water (The amount of degraded gasoline is controlled such that the concentrations of formic acid and acetic acid in the water after separation into two phases are 1,000 and 2,000 ppm, respectively.)
 Test condition: The above solution is sealed in cylindrical cups of the specimen sheets 30 mm in diameter, held at 45°C for 3 weeks, and the amounts of metallic elements eluted in the solution are measured.

Fig. 1 Relationship between Zn content in coating layer and dissolution of metals

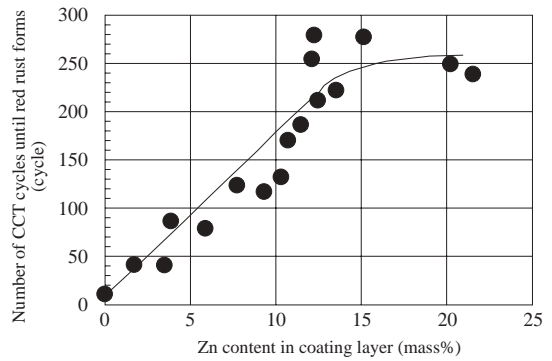


Fig. 2 Relationship between Zn content in coating layer and CCT cycles until red rust forms

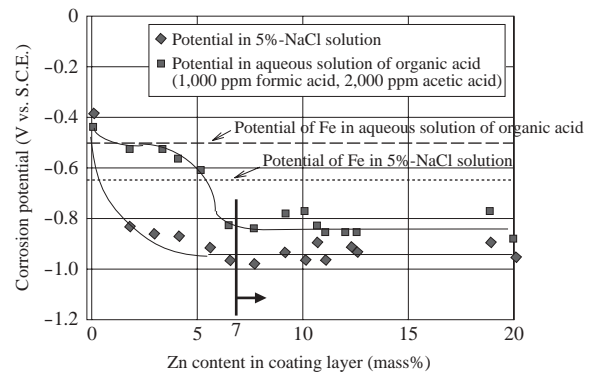


Fig. 3 Relationship between Zn content and dipping potential of coating alloy

tent increases, that of the steel substrate is inhibited. Through a combined corrosion test simulating a salt damage environment (1 cycle of salt water spray for 2 h → drying at 60 °C for 4 h → wetting at 50 °C for 2 h), it has been confirmed that the time before the occurrence of red rust becomes longer as the Zn content increases, as can be seen in Fig. 2.

With respect to electro-chemical analyses, Fig. 3 shows the measurement results of the change in the corrosion potential of the coating alloy in an aqueous solution of organic acid and a 5%-NaCl solution versus the Zn content. In salt water, when the Zn content in the coating layer is approximately 1.5 mass %, the electrochemical potential of the coating layer becomes lower (basier) than that of the steel sheet, and the potential becomes substantially constant as the Zn content increases to 4 mass % and further. In an organic acid solution, when the Zn content of the alloy is approximately 4 mass %, its potential becomes lower (basier) than that of the steel sheet. On the other hand, as seen in Fig. 4, whereas Zn is evenly dispersed as far as the Zn content in the coating alloy is equal to or less than the eutectic point, 9 mass %, coarse primary Zn precipitates in acicular crystals when the Zn content is 20 mass %. In other words, it is in the hyper-eutectic range. It has been made clear that the primary Zn phase begins to coarsen as the Zn content in the coating alloy increases to 11 mass % and beyond. As a result, it is presumed that the abrupt increase in the dissolution of Zn seen in Fig. 1 results from the selective dissolution of the coarse Zn crystals that have formed in the coating layer.

From the above, it is understood that the Sn-Zn coating alloy has

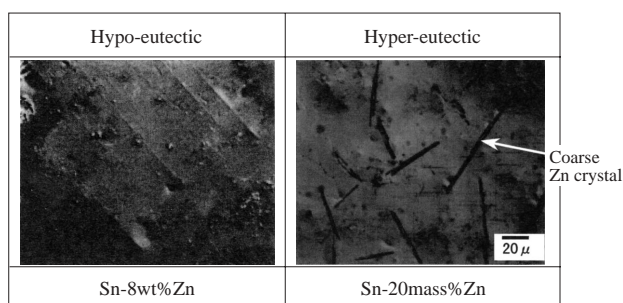


Fig. 4 Photomicrographs of Sn-Zn coating layers by electron microscope

an effect of a sacrificial anode in salt water or an organic acid solution if the Zn content is more than 4-5 mass %, but, if the Zn content exceeds 11 mass %, then coarse Zn crystals form and as a consequence, an excessive dissolution of Zn occurs. Based on the above understanding, the Zn content in the coating alloy was set, with an allowance for operational fluctuations, at 8 ± 1 mass % as an optimum value for minimizing the corrosion of the steel sheet in an environment of degraded gasoline and salt damage and at the same time, suppressing an excessive sacrificial anode effect.

3.2 Properties required of fuel tank material

The properties required of a fuel tank material explained below were evaluated using specimen steel sheets that have undergone a conversion coating treatment (deposition amount 20 mg/m^2)⁹⁾. Note that Nippon Steel has developed a conversion coating film not containing Cr^{6+} , which proved to have the same level of corrosion resistance as the one used in the evaluation, and has been made commercially available (no further explanations are given herein).

3.2.1 Press formability

3.2.1.1 Friction coefficient of coating alloy

To evaluate the lubricating properties of the coating alloy, the friction coefficient of the steel sheet was measured by Bowden's method (load 0.98 N, steel ball diameter 20 mm, sliding speed 0.5 m/min, no oil application). The results are shown in Table 1. Thanks to excellent characteristics of metallic Sn, the Sn-Zn coating alloy exhibited a lower friction coefficient than that of a terne sheet.

3.2.1.2 Deep drawability

Limiting drawing ratio was measured through Erichsen test (punch diameter 50 mm, punch shoulder radius 5 mm, clearance 1.4 mm, blank holding force 4,900 N, Idemitsu Kosan's Z3 oil applied). As seen also in Table 1, the Sn-Zn-alloy-coated steel sheet showed as good deep drawability as a terne sheet did.

3.2.1.3 Workability of coating alloy

From the measurement results of the friction coefficient and limiting drawing ratio, the Sn-Zn-alloy-coated steel sheet is expected to have good press formability. In the press forming work of a real fuel tank, however, a forming die assembly has a bead and as a consequence, the work condition is quite demanding. In view of this, a draw-bead test was carried out using an R type die assembly (bead shoulder radius 4 mm, die shoulder radius 2 mm) until the thickness reduction reaches 12 to 16% of the initial thickness. At the surface

Table 1 Dynamic friction coefficient and limiting drawing ratio

	Friction coefficient by Bowden's method	Limiting drawing ratio
Sn-9%Zn	0.19 (Without oil)	2.30 (With oil)
Terne sheet	0.57 (Without oil)	2.30 (With oil)

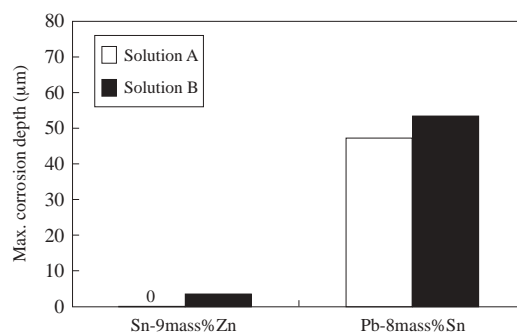


Fig. 5 Maximum corrosion depth in degraded gasoline

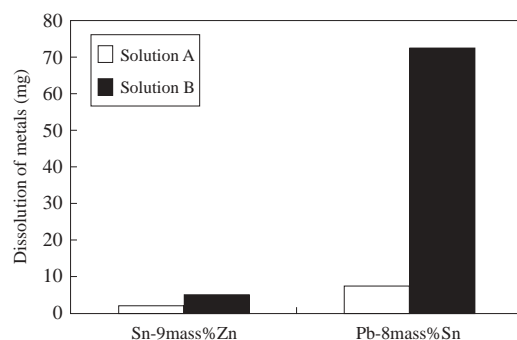


Fig. 6 Dissolution of metals in degraded gasoline

observation after the test, no damage to the coating metal to reveal the base steel sheet was found, and the press formability of the product was evaluated as good.

3.2.2 Corrosion resistance of inner surface

Specimen sheets were drawn into cylindrical cups (diameter 50 mm, contraction ratio 2.2), and were filled with 40 cm^3 of either of the following solutions A and B: regular gasoline + degraded gasoline + 10 mass % water, where, in the case of solution A, the water contained 100 ppm formic acid, 200 ppm acetic acid, and 100 ppm Cl, and, in the case of solution B, 1,000 ppm formic acid, 2,000 ppm acetic acid, and 100 ppm Cl. The cups filled with the solution were sealed, held at 45°C for 4 weeks, and then corrosion depth and metal dissolution were measured. As seen in Figs. 5 and 6, the corrosion tendencies of the two products in the solutions A and B were similar, and the developed Sn-Zn-alloy-coated steel sheet displayed corrosion resistance better than that of the terne sheet.

3.2.3 Corrosion resistance of outer surface

It is often the case that a fuel tank is installed suspended under the floor of a car body, and it is coated with black paint to ensure good appearance and resistance to salt damage. In the test of the authors, specimen sheets were coated with a black alkyd melamine resin paint (thickness $20 \mu\text{m}$) that is generally used for a tank of a terne sheet. No paint exfoliation was observed in the specimens of both the developed product and the terne sheet, either in a primary adhesion test (peeling with an adhesive tape of the paint coating that was cross cut in grids) or a secondary adhesion test (the same peeling after immersion in water at 40°C for 10 days). Fig. 7 shows the appearances of specimens formed into the shape of a real tank, seam welded and subjected to 120 cycles of a CCT consisting of salt spray, drying and wetting (1 cycle/day). The maximum corrosion depth of terne sheet specimens was 0.73 mm and that of Sn-Zn-coated steel

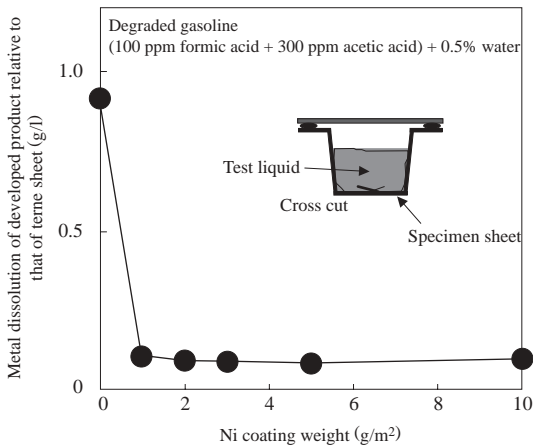


Fig. 10 Relation between Ni coating weight and corrosion resistance of inner surface

Table 2 Friction coefficient and limiting drawing ratio

	Friction coefficient	Limiting drawing ratio
GI + Ni	0.09	2.3
Terne sheet	0.10	2.3

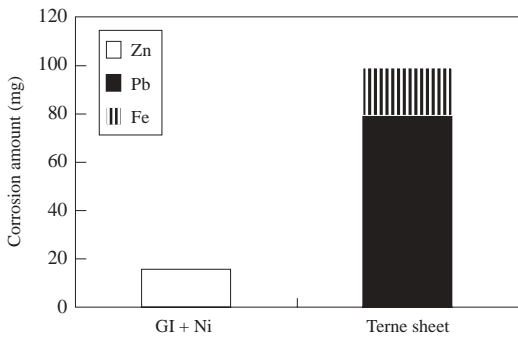


Fig. 11 Test results of corrosion resistance of inner surface

measured through a flat-die sliding test (load 49 N, sliding speed 20 m/min) and the limiting drawing ratio measured through a deep drawability test (punch diameter 50 mm, punch shoulder radius 4 mm, blank holding force 4,900 N), using oiled specimen sheets 1.0 mm in thickness. The results are shown in Table 2. The GI-Ni double-layered steel sheet exhibited a lower friction coefficient than and the same limiting drawing ratio as those of the terne sheet.

4.2.3 Corrosion resistance of inner surface

The corrosion resistance of inner surface was evaluated in the following manner: a test piece was formed into a hat shape 35 mm in height, its bottom surface was cross cut, the test piece was immersed in degraded gasoline kept at room temperature, containing 100 ppm formic acid, 300 ppm acetic acid and 0.5% water for 6 weeks, and the amounts of metal dissolution were measured. Fig. 11 shows the results. Whereas the dissolution of Pb and Fe was found with the terne sheet, the dissolution of Zn was found with the developed product, but its amount was far smaller than those of Pb and Fe of the terne sheet. Thus, the GI-Ni double-layered steel sheet proved to have better resistance to degraded gasoline than a terne sheet does.

4.2.4 Corrosion resistance of outer surface

Specimen sheets were coated with black alkyd melanin resin paint

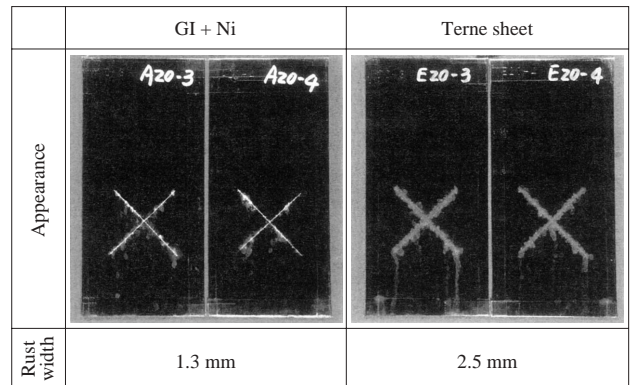


Fig. 12 Test results of corrosion resistance of outer surface with paint coating

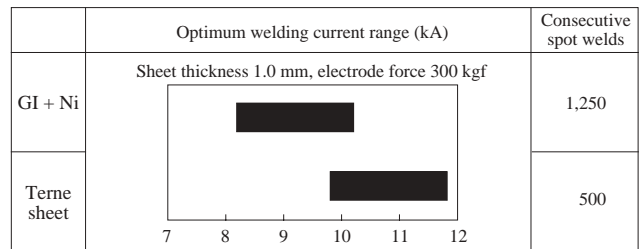


Fig. 13 Test results of spot weldability

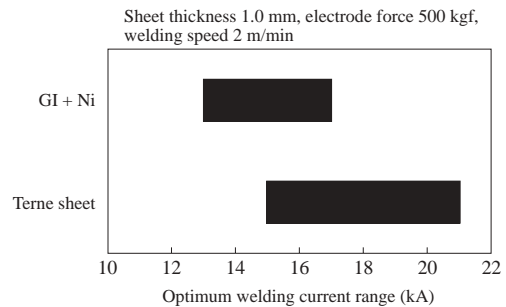


Fig. 14 Test results of seam weldability

(thickness 20 μm), cross cut, subjected to 90 cycles of a combined corrosion test according to JASO M609-91, and the maximum width of rust was measured. Fig. 12 shows the results. The rust that formed at the cross-cut portion of the GI-Ni double-layered steel sheet was white rust and its width was substantially the same as that of the terne sheet.

4.2.5 Spot weldability

Specimen sheets were spot welded using Cu-Cr dome electrodes having a tip diameter of 6 mm and a tip radius of 40 mm, and an optimum welding current range and the number of consecutive spot welds were measured. Here, the optimum welding current range was defined as the range from the current at which a nugget diameter equal to $4\sqrt{t}$ (t : sheet thickness) was obtained (lower limit) to that at which expulsion occurred (upper limit), and the consecutive spot welds were done at a welding current roughly in the middle of the optimum welding current range until the nugget diameter became smaller than the lower limit figure. Fig. 13 shows the results. The optimum welding current range of the GI-Ni double-layered steel

sheet was roughly the same as that of the terne sheet and its consecutive spot weldability was excellent.

4.2.6 Seam weldability

Specimen sheets were seam welded using Cu-Cr electrode wheels 9 mm in width and 15 mm in edge radius, and the optimum welding current range was measured, defining it as the range from the current at which a nugget diameter was equal to $2t$ (t : sheet thickness) (lower limit) to that at which expulsion occurred (upper limit). **Fig. 14** shows the results. The optimum welding current range of the GI-Ni double-layered steel sheet was a little narrower than that of the terne sheet, but it was well within a practically acceptable range. However, with the developed product, a Zn-Cu alloy formed on the electrode wheels during welding, penetrated into grain boundaries of the base steel sheet, and as a result, fine surface cracks developed. The authors have confirmed, however, that this could be prevented by taking the following measures related to the base steel and welding conditions: (1) inhibiting the penetration of the alloy by adding elements such as B to the base steel¹⁰⁾ and the like; (2) removing the Zn-Cu alloy from the electrode wheel surface with a cutting tool; and (3) decreasing the formation of the alloy on the electrode wheel surface by applying oil¹¹⁾.

5. Conclusion

For the purpose of reducing the use of environmentally hazardous Pb, the authors have developed two types of coated steel sheet products capable of replacing a terne sheet, namely, the hot-dip Sn-Zn-alloy-coated steel sheet produced by the molten flux using method and the GI-Ni double-layered steel sheet produced using an existing CGL for double-layer coating. Properties equal to or better than those of a terne sheet have been confirmed with both of the developed products. The new products are already being commercially used at carmakers, significantly contributing to the reduction of Pb in car manufacturing.

References

- 1) Home page of the Japan Automobile Manufacturers Association, 2001
- 2) Maki, J. et al.: J. of Surface Finishing Society of Japan. 51 (6), 653-658 (2000)
- 3) Maki, J. et al.: *Materia*. 39 (2), 178 (2000)
- 4) Sudoh, S: *Industrial Materials*. 45 (10), 94 (2000)
- 5) Sano, T. et al.: *Automotive Engineers*. 52 (7), 73 (1997)
- 6) Ogata, H. et al.: *Proc. of Automotive Engineers Convention*. No. 83-99, 1999, p.9
- 7) Warnecke, Wilhelm et al.: SAE Paper. 01, 1999
- 8) Hahn, H.N. et al.: SAE Paper. 971006, 1997
- 9) Izaki, T., Eguchi, H., Higuchi, S.: *CAMP-ISIJ*. 9, (1996)
- 10) Japanese Unexamined Patent Publication Tokukai. 2000-104180. Apr. 11, 2000
- 11) Japanese Unexamined Patent Publication Tokukai. 2001-219279. Aug. 14, 2000