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 automobile. 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 2005.

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
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[8], a hot-dip Al-coated steel sheet[7], a galvannealed steel sheet with organic coating films[4-6], 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 sheet[7] has been used in Europe, and a Zn-Ni-alloy-coated steel sheet with organic coating films[5] 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 content 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 ℃ for 4 h → wetting at 50 ℃ 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 (base) 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 (base) 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
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/m²). Note that Nippon Steel has developed a conversion coating film not containing Cr6⁺, 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 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 cm³ 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 µm) 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 specimens was 0.37 mm.
3.2.4 Welding and joining properties

3.2.4.1 Spot weldability

Fig. 9 shows the optimum welding current range that was measured using dome electrodes of alumina-dispersed copper having a tip diameter of 6 mm. The current at which a nugget diameter equal to 4 t (t: sheet thickness) was obtained was defined as the lower limit current, and that at which expulsion occurred as the upper limit. The Sn-Zn-coated sheet proved to have a wider welding current range than that of a terne sheet. Fig. 9 also shows the number of consecutive spot welds tested under a welding current of 0.9 times the upper limit current. The spot weld number of the Sn-Zn-coated sheet was smaller than that of the terne sheet. This is due to the fact that Sn or Zn in the coating layer is likely to form an alloy with Cu in the electrodes. A material having a small number of consecutive spot welds will require more frequent change of electrodes, and productivity is lowered. It turned out, however, that this could be improved by adequately controlling welding conditions (electrode force, welding time, and electrode shape).

3.2.4.2 Seam weldability

In a laboratory test, the optimum current range of the Sn-Zn-coated steel sheet was 3 kA, and its continuous welding length was more than 450 m. In a test fabrication of a real fuel tank using the developed product, the authors have confirmed a continuous welding length equal to that of a terne sheet.

4. GI (hot-dip zinc plating)-Ni Double-layered Steel Sheet

4.1 Concept of product development

Besides the terne sheet, a zinc-coated steel sheet (electro-galvanized steel sheet, galvannealed steel sheet or the like) also has long been used as the material of an automobile fuel tank; it is another Pb-free material for a fuel tank. The resistance to degraded gasoline of a zinc-coated steel sheet, however, has been known to be insufficient. In view of the situation, the authors studied electrolytic coating of an additional layer on the surface of an economically advantageous hot-dip galvanized steel sheet (GI) for solving the problem. Among the metallic elements that can be electrolytically deposited, Sn, Ni and the like have been known to have good resistance to degraded gasoline. The authors opted for Ni for reasons such as the ease in coating weight control and the stability of a plating bath, and developed a GI-Ni double-layered steel sheet. The developed product can be produced using one of Nippon Steel’s existing CGLs for double-layered galvanized steel sheets and as a consequence, is characterized by being economical.

4.2 Product characteristics

4.2.1 Coating structure

In consideration of formability, weldability and other required properties, the Zn coating weight of the developed product was set at 45 g/m², a figure with most of coated steel sheets for automotive use. The coating weight of Ni was determined through tests of the corrosion resistance of inner surface. As seen in Fig. 10, resistance to degraded gasoline is enhanced when the coating weight of Ni is 1 g/m² or more, and with a safety allowance, the Ni coating weight of the developed product was set at 5 g/m². In addition, for the purpose of improving the corrosion resistance of outer and inner surfaces and formability, coating films not containing Cr⁶⁺ were formed on the surfaces of the Ni coating layers.

4.2.2 Press formability

Press formability was evaluated based on the friction coefficient
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 melamin resin paint (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 4t (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 steel\(^{10}\) 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 oil\(^{11}\).

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

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