NIPPON STEEL TECHNICAL REPORT No. 57 APRIL 1993

UDC669.146.9 : 629.11.011.6

Development of Precoated Steel Sheets for Automotive Use

Yasuhiko Miyoshi*1
Hisao Odashima*1
Yoshio Shindo*1
Makoto Yoshida*1
Tatsuya Kanamaru*1

Abstract:

Development of precoated steel sheets for automotive use in the past eight years is described. Detailed examinations of disassembled field automobiles revealed that the perforation corrosion of the door hem flange occurs not in the upper part of the hem flange as traditionally claimed, but in crevices between the lapped door panels. This result shows that the perforation corrosion resistance of precoated steel sheet depends on its unpainted corrosion resistance in the special environment of crevice. Four new types of precoated steel sheet were developed. DURGRIP-E has excellent cratering resistance during cathodic electrodeposition and provides high press formability as well. The thin-film organic composite-coated steel is a sheet product whose press formability is improved by decreasing the thickness of the organic film to about 1 μm without sacrificing weldability. Further progress is expected of the Zn-Cr alloy-electroplated steel sheet featuring high corrosion resistance despite low coating weight. Tin-coated 5% chromium steel sheet was developed as a new material for alcohol fuel tanks.

1. Introduction

Number 315 of the Seitetsu Kenkyu (1984), a special issue on precoated steels, carried many papers on corrosion resistant steel sheets for automobiles. The subsequent eight years have seen remarkable advance in Nippon Steel's automotive surface treatment technology.

First, research was deepened on the corrosion mechanism of automobile bodies. The corrosion mechanism of automobile bodies, or the corrosion resistance mechanism of zinc-coated steel sheets, was clarified through investigation made into field cars in which zinc-coated steel was used in large amounts, as well as by laboratory tests. Then, a technique was proposed for estimating the service life of automobiles from the clarified corrosion mechanism. This research is expected to provide guidelines for the development of new corrosion resistant automotive steel sheets.

Corrosion of painted zinc-coated steel was also studied in detail, which resulted in clarifying the importance of behavior of the zinc-iron alloy layer in the microscopic region at the front of underfilm corrosion.

Second, new precoated steel sheets were developed in response to automakers' five to ten-year innovation programs. Since DUREXCELITE (Zn-Fe two-layer alloy-coated steel),

*1 Technical Development Bureau

DURZINKLITE (Zn-Ni alloy-coated steel), DURGRIP (galvannealed steel), and Nittetsu Welcote-N (prepainted Zn-Ni alloy-coated steel) were expected to decline in press formability and weldability, if their coating weight was increased for the purpose of improving corrosion resistance, new types of precoated steel sheets were developed with enhanced corrosion resistance without sacrificing press formability and weldability. They are DURGRIP-E and thin-film organic composite coated steel. Zn-Cr alloy-coated steel falls in the same category in the sense that it is low in coating weight but high in corrosion resistance.

Edge corrosion protection and as-painted image clarity have gained importance in recent years. Technology has been developed to manufacture precoated steel sheets that meet such requirements. The increasing severity in the body corrosion protection requirement had the effect of raising the target level of exhaust system corrosion protection. As a result, the conventional Al sheet (hot-dip aluminum-coated steel sheet) and stainless steel are being replaced by aluminum-coated stainless steel sheet.

Third, with an eye to a future fuel shift from gasoline to alcohol, research is under way on the development of tin-coated 5% chromium steel sheet as a fuel tank material resistant to corrosion by the alcohol fuel.

Among the technical developments mentioned above, the field service life estimation of zinc-coated sheet and the research and development results of DURGRIP-E, thin-film organic composite-coated sheet, Zn-Cr alloy-coated sheet, and tin-coated chromium sheet are described here. For the conventional precoated steels for automobiles, refer to previous publications[1-3].

2. Field Service Life Estimation of Zinc-Coated Steel Sheet for Automobile Body

2.1 Results of field car disassembly investigation

Automobile body corrosion in the snow-belt region is known to be the severest in the door hem flange. **Photo 1** shows the results of microscopic investigation of a door from a 10-year field service car[4]. The degree of corrosion differs within the same door. Perforation corrosion occurred not in the open area at the top of the hem as traditionally thought, but in the steel sheet lap in the hem. A door of a 4.5-year field service car with inner and outer panels of zinc-coated steel with a coating weight of about 90 g/m^2 was examined in detail by using such instruments as an optical microscope and an X-ray microanalyzer. Where some

Photo 1 Corrosion of door hem flange of automobile run for 10 years in snow-belt region

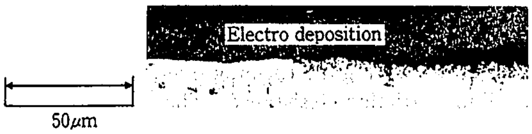

Photo 2 Corrosion of door hem flange, made of 90 g/m^2 zinc-coated steel, of automobile run for 4.5 years in snow-belt region

paint penetrated into the hem or where sealant or adhesive was locally deposited, the corrosion of the zinc coating covered by such substances was relatively low in severity (see **Photo 2**).

In other words, the door hem is severely corroded and liable to perforation where it is not covered with paint film or sealant. The perforation corrosion resistance of zinc-coated steel sheet is thus known to depend on its corrosion resistance in the bare or unpainted condition. The door hem area of the 4.5-year field service car showed little or no red rust, but the zinc coating was completely lost by corrosion in some portions. This finding puts the field service life of the 90-g/m^2 zinc coating at a minimum of 4.5 years.

2.2 Field service life estimation

Specimens were prepared by lapping two steel sheets with a certain gap to simulate hem corrosion and were cyclic corrosion tested. Specimen shape and test conditions were the same as previously reported[5]. **Fig. 1** shows the test results for different zinc coating weights[4]. As indicated, the corrosion depth linearly increases with test time. The line for the cold rolled steel sheet passes through the origin, and the 0.7-mm thick cold rolled sheet is perforated in 55 cycles. Since the field service life of the cold rolled steel sheet is said to be about 2.5 years, 55 cycles of this cyclic corrosion test can be equated with 2.5 years of field service life.

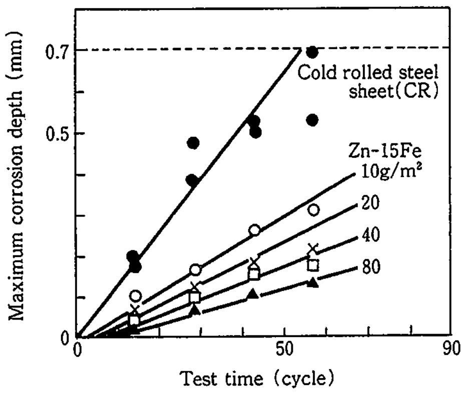

Fig. 1 Cyclic perforation corrosion test results of lapped panel specimens

The lines for the zinc-coated steel sheets do not pass through the origin. This means the presence of a certain incubation period. Since the incubation period increases with increasing zinc coating weight, only the zinc coating is considered to be corroded during that period. Each line starts to rise immediately after the incubation period. The line gradient is smaller than for the cold rolled steel sheet, and decreases with increasing zinc coating weight. Even after the complete loss of the zinc coating, the corrosion behavior of the substrate steel is different from that of the cold rolled steel sheet. This tendency is characteristic of lapped panel specimens. With simple flat panel specimens, the substrate steel begins to corrode at the same rate as the cold rolled steel sheet after the inculation time.

When the lapped panel specimens were opened and observed, they were found to have corroded not generally but locally, showing both corroded steel substrate and remaining zinc coating layer from place to place. It was also found that the zinc-containing corrosion products did not easily run out of the lapped panel specimens but covered the steel surface over a long period of time.

The galvanic protection of the zinc coating and the protective action of the zinc-containing corrosion products are considered responsible for the low corrosion rate of the substrate steel as compared with the cold rolled steel sheet. With actual automobiles, corrosion is localized as shown in **Photo 1**. Since the corrosion products are expected not to easily flow out of the hem flange, the same phenomena are considered to occur as observed with the lapped panel specimens.

The field service life of 90 g/m^2 Zn-15%Fe alloy-coated steel is estimated as shown in **Fig. 2** according to the above-mentioned survey results and experimental results. The service life of the cold rolled steel sheet (line ①) is 2.5 years. The incubation period of the zinc-coated steel is 4.5 years according to field survey results. The field service life line of the zinc-coated steel rises after the incubation period, and is not line ② which is parallel to line ①, but is line ③. The slope of line ③ is obtained by multiplying the slope of line ① by the ratio of the slope of the line for the 80 g/m^2 zinc coating to that of the line for the cold rolled steel.

Corrosion of the zinc-coated steel sheet initially proceeds along line ③ and is predicted to proceed along line ④ parallel to line ① after the period during which the zinc coating and zinc-containing corrosion products are lost. In other words, the perforation corrosion of the hem flange proceeds in three stages as shown in **Fig. 2** before perforation takes place.

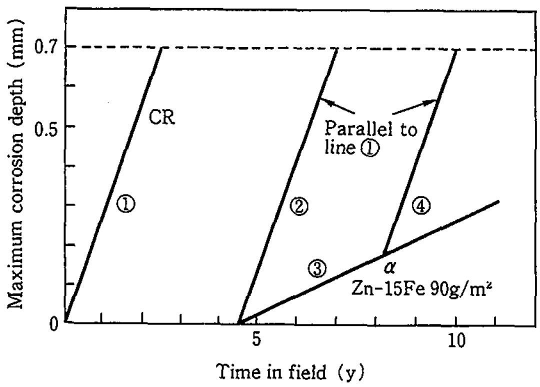

Fig. 2 Estimated field service life of door hems made of 90-g/m^2 zinc-coated steel

3. Properties of New Corrosion Resistant Steels Developed for Automobile Body

3.1 DURGRIP-E

Zn-Fe alloy-coated steel sheet has been widely used as automobile body panels on the strength of excellent corrosion resistance particularly after painting. In recent years, user demand for heavier coating is mounting with rising levels of corrosion protection targets. As a result, demand is soaring for DURGRIP which can be easily manufactured with large coating weights. This precoated steel product had a drawback in susceptibility to the paint film defect called craters during cathodic electrodeposition. This problem, however, was solved by depositing an Fe-Zn alloy with an iron concentration of 75 to 85% as an upper layer, through the application of the DUREXELITE coating technology. **Fig. 3** shows the effect of the upper layer coating in improving the appearance of the cathodically electrodeposited primer[6]. This type of coated steel was designated DURGRIP-E.

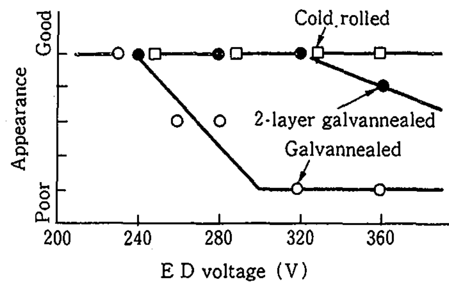

Fig. 3 Effect of upper layer in inhibiting cratering of cathodically electrodeposited primer

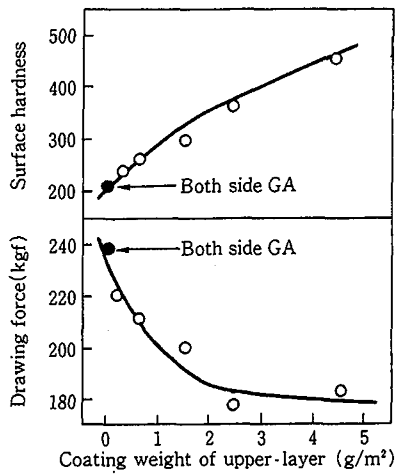

Fig. 4 Relationship between upper-layer coating weight and surface hardness of DURGRIP (galvannealed steel)

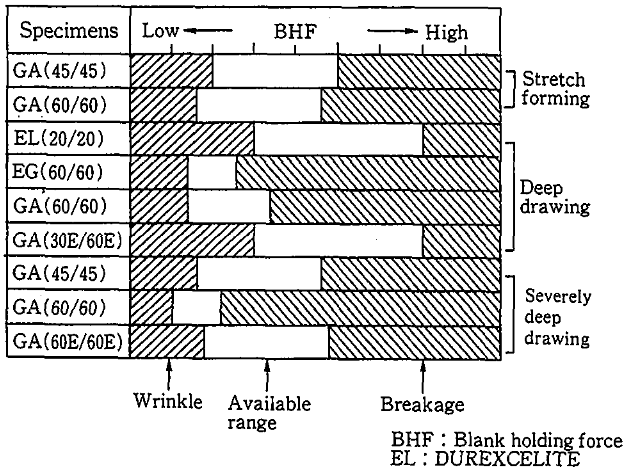

Fig. 5 Press forming test results of various Zn-Fe alloy-coated steels

Generally, precoated steel sheet has greater sliding friction resistance than cold rolled steel sheet. A high sliding friction resistance obstructs metal flow during press forming and reduces the press formability of the precoated steel. This tendency increases with increasing metal coating weight. A hard surface layer may be deposited to improve the situation. A hard surface layer is difficult to deform during the forming operation and acts to reduce the sliding friction resistance. The upper layer of DURGRIP-E is high in hardness and lowers the sliding drawing force, as shown in **Fig. 4**[7]. (The drawing force during the drawing test can also be lowered.) As a result, the optimum blank holding force on the automobile production line increased in range, making it possible to press form DURGRIP-E with heavy coating weight.

Fig. 5 shows the optimum blank holding force range for various types of precoated steel sheet. The range narrows with increasing coating weight, but can be expanded through the deposition of an upper layer[7].

DURGRIP-E was developed originally to improve paintability, but was found also to have improved press formability. It now finds a wide field of application where good press formability is a prime consideration.

3.2 Thin-film organic composite coated steel

3.2.1 Solvent-based paint

Conventional organic composite coated steel sheet contained metal powder in the organic film to impart electric conductivity for spot weldability. The hard metal powder often caused die galling during press forming, resulting in forming defects. A new thin-film organic composite coated steel sheet was developed that had the organic film thickness reduced from 5.5 to 1 μm to eliminate the addition of metal powder. The 1-μm thick organic film is partially destroyed by the electrode force during spot welding and exhibits sufficient electric conductivity. The loss of corrosion resistance due to the reduction of organic film thickness is made up for by improving the paint resin, adding silica powder as pigment, and increasing the Zn-Ni alloy coating weight from 15 to 20 g/m^2.

Fig. 6 shows the plain corrosion resistance of organic composite coated steel sheets with solvent-based paint film[8]. The new thin-film organic composite coated steel sheet performs better than the conventional one (Nittetsu Welcote-N). **Fig. 7** shows its die galling characteristics as evaluated by the tape test of die surfaces after cup drawing[7]. A paint film thickness of 0.8 μm or more provides satisfactory die galling characteristics.

3.2.2 Water-born paint

Water-born paint with water-dispersible resin is also applied. Since such water-dispersible resins invariably contain many hydrophilic functional groups, water-born paints were inferior to solvent-based paints in corrosion protection. This disadvantage, however, has been eliminated through technical development. The thin-film organic composite coated steel sheet using water-born paint is advantageous from the viewpoint of pollution control as it is low in organic solvent consumption, as well as in terms of spot weldability.

The consecutive spot weldability is shown in **Fig. 8**. The minimum number of spot welds that can be continuously made with the thin-film organic composite-coated steel is 5,000 under these test conditions. Specimens were machined from the skirt area of production doors made of cathodically primed precoated steel sheets and were evaluated for hem corrosion resistance. The results are given in **Fig. 9**[9]. The hem perforation corrosion resistance of the thin-film organic composite coated steel sheet is much higher than that of the Zn-Ni alloy-coated steel.

Both the solvent-based and water-born paint types are extensively used in automotive body panels. These are cases where the Zn-Ni alloy coating weight is increased to 30 g/m^2 for improving corrosion resistance.

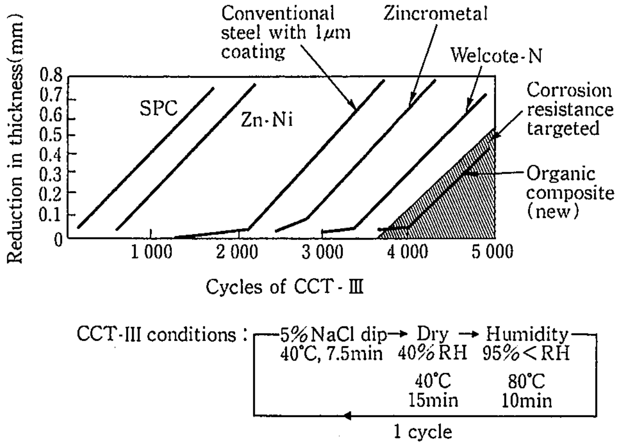

Fig. 6 Plain corrosion resistance of solvent-based paint-coated thin-film organic composite coated steel

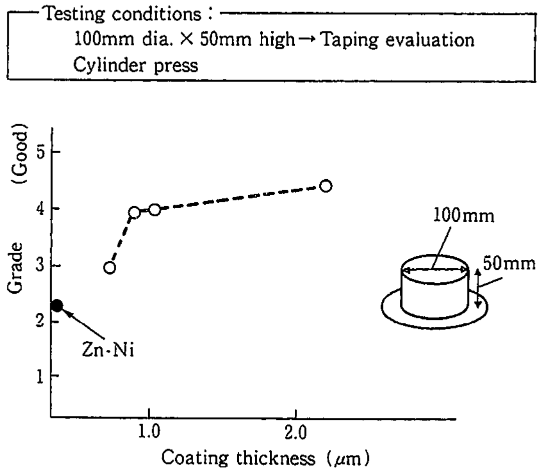

Fig. 7 Press die galling behavior of solvent-based paint-coated thin-film organic composite coated steel: Results of tape test on die surface after cup drawing

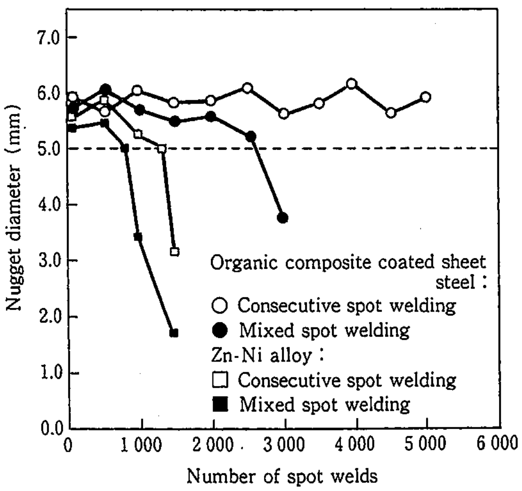

Fig. 8 Consecutive spot weldability test results of water-born paint-coated thin-film organic composite coated steel

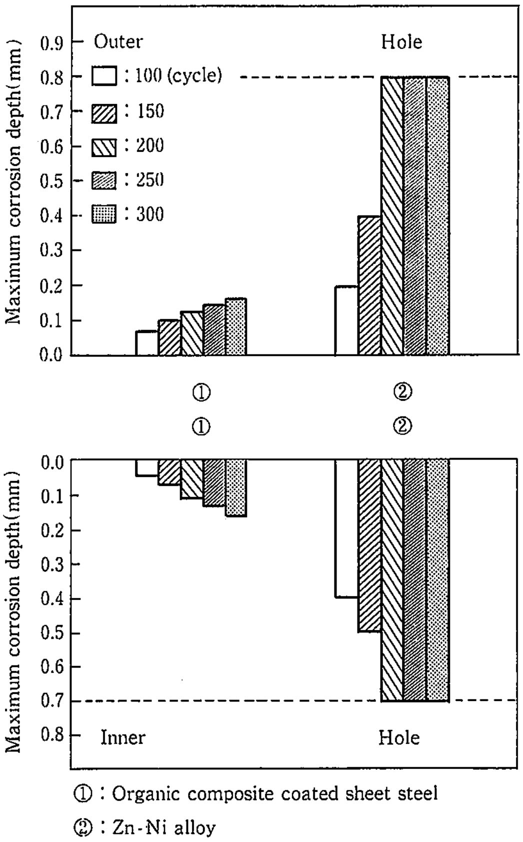

Fig. 9 Corrosion resistance of skirt areas of production doors made of ED primed thin-film organic composite coated steel

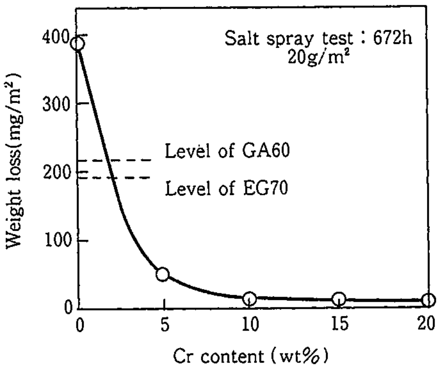

Fig. 10 Improvement in corrosion resistance of zinc-coated steel with addition of chromium

3.3 Zn-Cr alloy-electroplated steel sheet

Zinc-coated steel sheet exhibits excellent corrosion resistance thanks to the protective action of corrosion products that are formed on the steel surface in a corrosive environment and composed mainly of $Zn(OH)_2$ or $ZnCl_2 \cdot 4Zn(OH)_2$. The corrosion resistance of the zinc-coated steel sheet increases further with the addition of chromium to the zinc coating and markedly improves when 10% or more chromium is added, as shown in **Fig. 10**[10]. This improvement may be attributed to the protective action of the corrosion products that contain both zinc and chromium. Nickel has a similar beneficial effect. Since nickel is electrochemically more noble than iron, however, the Zn-Ni alloy coating assumes a more noble potential than the steel substrate when left to stand for a long period of time in a corrosive environment. In that case, it loses the galvanic protection to the steel substrate and becomes less protective against corrosion.

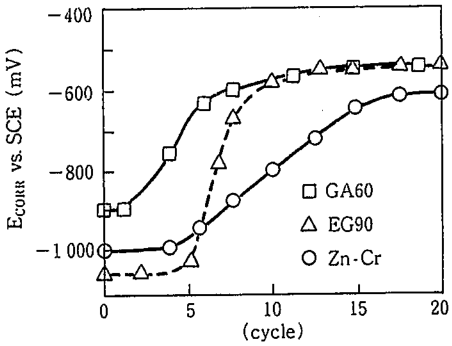

Fig. 11 Change in corrosion potential with time of zinc-coated steels in cyclic corrosion test (CCT)

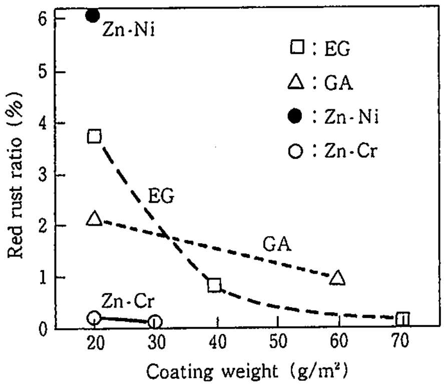

Fig. 12 Edge corrosion protection of zinc-coated steels in CCT

Chromium is easily passivated in air and normally exhibits a more noble potential than iron, but is essentially a less noble metal than iron. When added to the zinc coating, chromium exhibits its essential potential as can be seen in **Fig. 11.** The potential of the Zn-Cr alloy coating is thus close to that of pure zinc[10]. When left to stand in the CCT environment, the zinc coating (EG90) and the Zn-Fe alloy coating (GA60) are dissolved and lost in a short time, exposing the steel substrate and exhibiting the potential of iron. On the other hand, the Zn-Cr alloy coating has superior corrosion resistance, and is low in the dissolution rate and takes a long time to reach the potential of the steel substrate. Unlike the Zn-Ni alloy coating, the Zn-Cr alloy coating always maintains a less noble potential than iron and thus keeps its galvanic protection over the steel substrate.

As discussed above, the Zn-Cr alloy coating forms a highly corrosion resistant film of corrosion products and exerts a galvanic protection effect on the steel substrate while slowly dissolving. It is a very convenient coating from the point of view of corrosion protection. It exhibits excellent corrosion resistance even at a low coating weight. When the Zn-Cr alloy coating was tested for edge corrosion protection, it performed far better than the Zn-Ni alloy coating, Zn-Fe alloy coating and Zn coating with the same coating weight[11].

Conventional chromium electroplating normally utilized electrodeposition from Cr^{6+}. Plating of chromium as an alloy with zinc calls for an electrodeposition technique from Cr^{3+}. Membrane and induced codeposition are usually applied as such techniques. The present study is characterized by the production of a Zn-Cr alloy coating by the use of additives.

The Zn-Cr alloy can be applied also as undercoating for the aforementioned thin-film organic composite coated steel sheet. In that case, nickel is usually added to the Zn-Cr alloy coating[12].

4. Corrosion-Resistant Steel Sheet for Alcohol Fuel Tanks

4.1 Corrosion of various metals in methanol fuel

Methanol is highlighted as a substitute for gasoline and is already used commercially in some areas. This fuel, however, badly corrodes terne-coated (lead-tin alloy-coated) steel sheet, the current fuel tank material. An attempt was made to develop a substitute corrosion resistant material for methanol fuel tanks. In service, methanol tends to oxidize into formaldehyde and formic acid, which are considered to accelerate the corrosion of the fuel tank metal. Therefore, various metals were immersion tested in methanol with and without such compounds.

The results are given in **Fig. 13**. As shown, iron, zinc, and aluminum-silicon alloy were badly corroded, while tin and nickel were corroded less severely[13]. The corrosion products of iron were mostly iron formate, and formic acid was found to promote the corrosion of the test metals according to the results of **Fig. 13**. Subsequent tests were therefore conducted in formic acid-containing methanol.

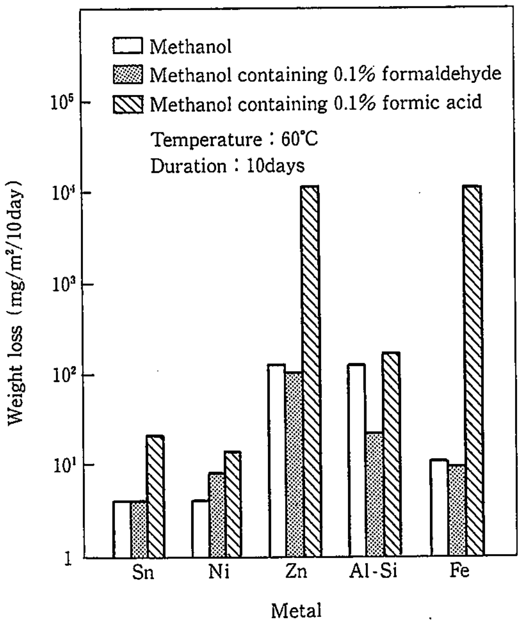

Fig. 13 Immersion corrosion test results of metals in methanol with and without formaldehyde and formic acid

4.2 Corrosion resistance of tin-coated 5% chromium steel

From **Fig. 13**, tin-coated or nickel-coated steel is expected to have good corrosion resistance in methanol. However, measurement of coupling corrosion current of the test specimens in formic acid-containing methanol revealed that tin and nickel both have more noble potential than the steel substrate and provide no galvanic protection for the substrate. This suggests the possibility that the steel substrate is corroded through coating defects in tin-coated or nickel-coated steel. Then, steel with chromium added to shift its potential toward the noble side was tested for corrosion in methanol. The test results indicate that the chromium content of the steel substrate should be 5% or more for the tin coating and be 11% or more for the nickel coating.

Fig. 14 shows the corrosion test results of tin-coated steel sheets with different chromium contents. As evident from the figure, the tin-coated 5% chromium steel has good corrosion resistance as methanol fuel tank material[14].

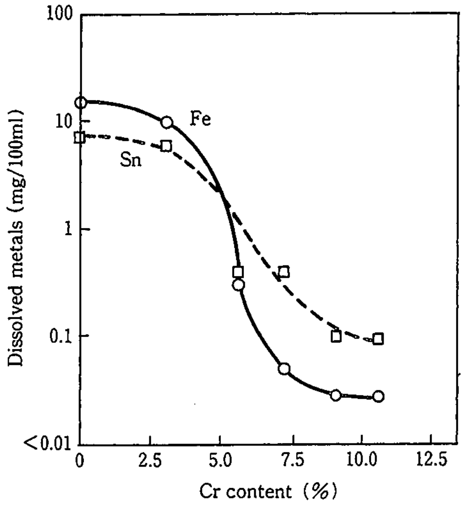

Fig. 14 Immersion corrosion test results of tin-coated chromium steels in methanol containing 0.1% formic acid

5. Conclusions

While discussing about the new types of precoated steels, it is keenly felt anew that the technology of precoated steels for automotive use has made remarkable progress in the past eight years. This is the result of incessant efforts on the part of not only steel coating researchers, but also field production engineers and headquarter staff. In this field, many manufacturers fiercely compete with each other, and strong user needs are expected to continue for some time. Not content with past achievements, we will continue on our research in pursuit of innovation.

References

1) Asamura, S.: Tetsu-to-Hagané. 77 (7), 861 (1991)
2) Miyoshi, Y.: Trans. Iron Steel Inst. Jpn. 31 (1), 1 (1991)
3) Kanamaru, T.: 138th and 139th Nishiyama Memorial Lecture, Tokyo, 1991, Iron and Steel Institute of Japan, pp. 165-210
4) Miyoshi, Y. et al.: Proc. GALVATECH '92, Amsterdam, September 1992, CRM, p. 528
5) Miyoshi, Y. et al.: SAE 840210, 1984
6) Soshiki, Y. et al.: Proc. GALVATECH '89, Tokyo, September 1989, Iron and Steel Institute of Japan, p. 329
7) Numakura, Y. et al.: SAE 900509, 1990
8) Shindou, Y. et al.: STEEL 90, Report 6, Genoa, 1990, United Nations
9) Odashima, H. et al.: SAE 920172, 1992
10) Suzuki, S. et al.: CAMP-ISIJ. 4 (5), 1601 (1991)
11) Kanamaru, T. et al.: Proc. GALVATECH '92, Amsterdam, September 1992, CRM, p. 331
12) Yamazaki, F. et al.: CAMP-ISIJ. 4 (5), 1603 (1991)
13) Higuchi, S. et al.: Tetsu-to-Hagané. 76 (8), 1325 (1990)
14) Mizuguchi, T. et al.: IXth Int. Symp. Alcohol Fuels, 1991, p. 830