

Development of Sn-Zn Coating Steel Sheet for Automotive Fuel Tanks, ECOKOTE-S

Masao KUROSAKI* Yasuto GOTO
 Shinichi YAMAGUCHI Yusho OYAMA
 Toshinori MIZUGUCHI Teruaki IZAKI

Abstract

Coating steel sheet for fuel tank which does not contain hazardous substances, durable for FAME (Fatty Acid Methyl Ester), possesses longer useful life has been demanded. ECOKOTE-S has been developed by modifying coated layer's structure of ECOKOTE-T, having finely dispersed zinc, attributed to superior corrosion resistance. ECOKOTE-S has pressing, welding and painting ability equivalent to existing materials, contributing to widely adoption by domestic and foreign automotive manufacturers.

1. Introduction

The automotive fuel tank is an important safety-related item that is required to meet stringent safety and environmental standards. About two-thirds of the automotive fuel tanks produced in Japan are made from steel sheet. Nippon Steel Corporation, which supplies a majority of steel sheets for automotive fuel tanks, has been developing new steel materials that suit the latest needs arising from the changing environment and trends of the automotive industry.

Fig. 1 outlines the development of new materials for automotive fuel tanks in Japan. Initially, Nippon Steel Corporation developed TERNESHEET,¹⁾ which was an improved edition of the Pb-Sn-plated steel sheet (terne-coated steel sheet) developed in the United States. Around 1990, however, the regulations on environmentally hazardous substances became more stringent, calling for the development of Pb-free steels. In the second half of the 1990s, the company started producing a Sn-Zn-coated steel sheet (ECOKOTE-T) and an aluminized steel sheet (ALSHEET[®])²⁾ as successors to TERNESHEET. ECOKOTE-T was “completely free of environmentally hazardous substances,” made “an automotive fuel tank boasting superior internal and external corrosion resistance,” and had “excellent workability (press formability, weldability, and paintability) almost comparable to that of TERNESHEET.” Because of those advantageous features, ECOKOTE-T was widely used by au-

tomakers, especially domestic ones.³⁻⁵⁾

At the turn of the century, the prolongation of the service life of automobiles (U.S. LEV-II Regulation: Guarantee of 15 years or 150,000 miles) necessitated the improvement of the salt damage corrosion resistance of fuel tanks and the compliance of the tank's internal corrosion resistance with new types of fuels such as etha-

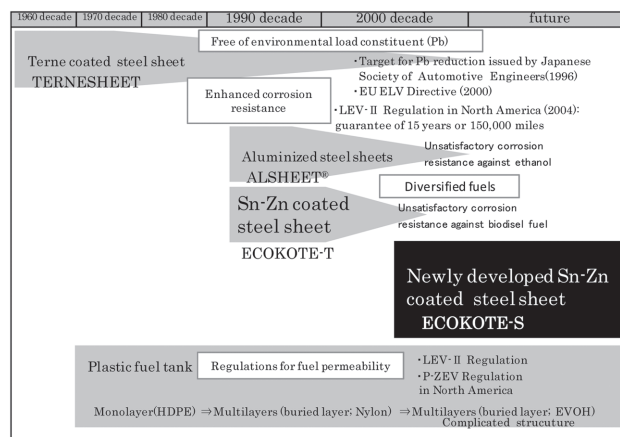


Fig. 1 Chronological development of automotive fuel tank materials

* Chief Researcher, Dr.Eng., Yawata R&D Lab.
 1-1, Tobihata-cho, Tobata-ku, Kitakyushu, Fukuoka 804-8501

nol-blended gasoline and biodiesel oil (light oil blended with fatty acid methyl ester). Under these conditions, we undertook the development of an improved form of ECOKOTE-T focusing on the microstructure of its coating metal layer and its corrosion behavior. Recently, we developed the technology for controlling the solidification structure of the coating metal layer, thereby improving the corrosion resistance of the steel sheet without changing the coating metal layer composition.

This report describes the solidification structure control technique applied to a Sn-Zn-coated steel sheet having a controlled coating metal layer microstructure (ECOKOTE-S) and the properties of the new product.

2. Coating Metal Microstructure and Solidification Behavior of Sn-Zn

2.1 Microstructure of the coating metal of ECOKOTE-S and ECOKOTE-T

Fig. 2 compares the microstructure of the coating metal layer of ECOKOTE-S and ECOKOTE-T, and Fig. 3 shows an equilibrium phase diagram of a Sn-Zn alloy.⁶⁾ Both coating metal layers have the composition of Sn-7mass%Zn, good ductility, and the benefits of the properties of Sn having a barrier-type anticorrosion mechanism and of Zn having sacrificial anticorrosion capability. In order to prevent the crystallization of primary Zn, the coating metals were given a hypoeutectic composition—a Zn content that is smaller than that of a eutectic composition (Sn-8.8mass%Zn).⁷⁾

In ECOKOTE-T, the proportion of primary Zn relative to the quantity ratio in the equilibrium phase diagram is not observed even

though it has a hypoeutectic composition. Instead, the entire coating metal layer appears to have a eutectic structure that reveals grains of Zn about 10 μm in size in the parts corresponding to the grain boundaries. It was found that those Zn grains could pass through the coating layer to reach the matrix and cause the corrosion resistance to decline.

On the other hand, the coating metal layer structure of ECOKOTE-S is a Sn-Zn eutectic structure lying between the dendritic phases of the primary Sn crystals. Thus, it corresponds to the structure shown in the phase diagram.

2.2 Directional solidification test

As described above, the coating metals of ECOKOTE-T and ECOKOTE-S have the same composition. However, there is a marked difference between them. In order to clarify the reason for this difference, we examined the solidification behavior of Sn-Zn basically by a directional solidification test. Using the Sn-Zn eutectic composition, Sn-8.8mass%Zn, as a reference, we observed the microstructures of the coating metals while changing the directional solidification of the alloys from hypoeutectic to hypereutectic.⁸⁾

Fig. 4 shows the solidification structure of the Sn-7.9mass%Zn hypoeutectic composition. The structure is completely eutectic showing no primary crystals of Sn. Zn appears in the part corresponding to the grain boundary.

Fig. 5 shows the influence of the coating metal composition and growth rate on the solidification structure. There exists a relatively wide region of the so-called coupled zone where only the eutectic structure can be observed despite the fact that the alloy composition is a hypoeutectic region. The solidification structure in the coupled

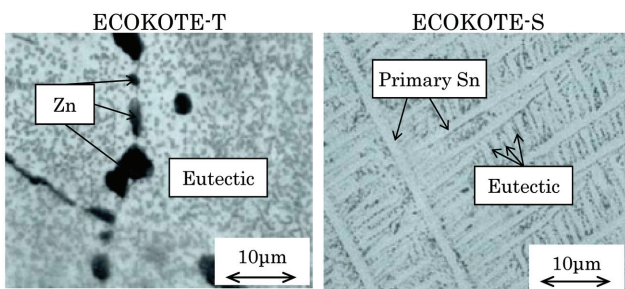


Fig. 2 Comparison of the microstructures of the coating metal

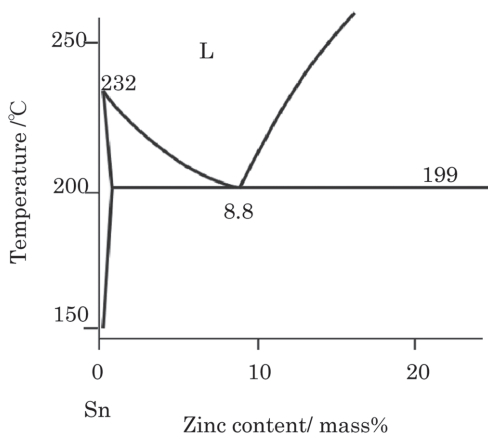


Fig. 3 Part of equilibrium phase diagram of tin-zinc alloy

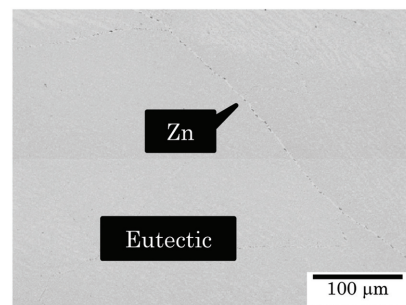


Fig. 4 Optical microscope images of the solidified structure on the horizontal cross section (Sn-7.9mass%Zn, V: 83μm/s)⁸⁾

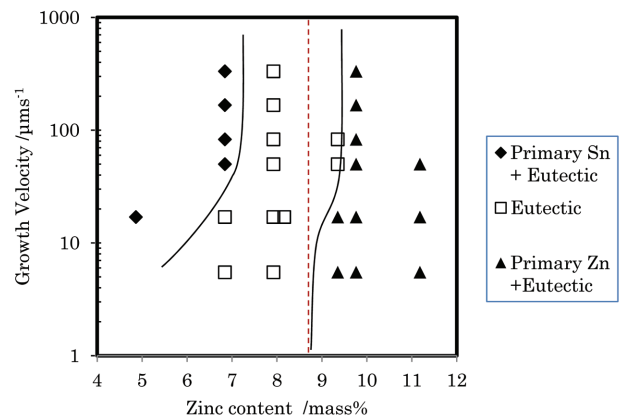


Fig. 5 Coupled zone of the Sn-Zn eutectic⁸⁾

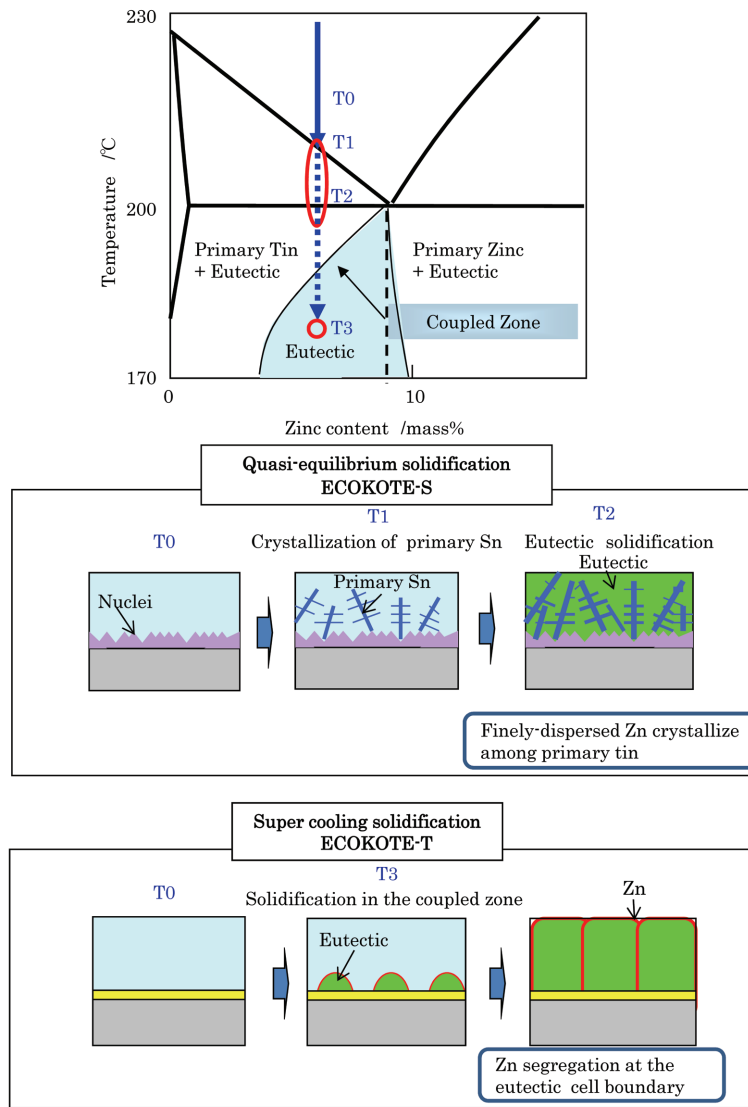


Fig. 6 Estimated solidification process ECOKOTE-S and ECOKOTE-T

zone is similar to the coating metal layer structure of ECOKOTE-T.

2.3 Controlling the coating metal layer structure

Fig. 6 shows the ECOKOTE-S/ECOKOTE-T solidification processes that were estimated from the results of the directional solidification test. In the case of ECOKOTE-T, undercooling occurred because of the smooth interface between the steel sheet and the coating metal, and the solidification structure deviated from the one shown in the equilibrium phase diagram. This may be the cause of the segregation of coarse grains of Zn.

To prevent Zn segregation, a special pretreatment was applied to the steel sheet before the hot-dip plating to form a steel sheet-coating metal interface that facilitated the crystallization of primary Sn, thereby crystallizing the primary Sn in the form of a dendrite. Then, the coating metal structure was controlled so that the Sn-Zn eutectic solidified, preventing the crystallization of coarse Zn grains. This paved way for stable production of ECOKOTE-S, which has a coating metal structure in which Zn grains less than 1 μm in size are finely dispersed (Fig. 2, right panel).

3. Study of ECOKOTE-S Properties

The essential properties required of materials for the manufacturing of automotive fuel tanks are as follows: (1) interior corrosion resistance, (2) exterior corrosion resistance, (3) weldability (resistance welding, etc.), and (4) press formability. As mentioned earlier, the automotive fuel tank is an important safety-related item. Because a fuel leak caused by corrosion failure of the fuel tank can lead to a serious accident, corrosion resistance is the most important material property. In terms of interior corrosion resistance, of particular importance is the corrosion resistance of the tank in a corrosive atmosphere containing organic acids, such as formic acid and acetic acid, that are produced when the fuel deteriorates (oxidation deterioration). In general, the automotive fuel tank is installed at the bottom of the car body; hence, it may be exposed to a severe corrosive environment containing de-icing agents, etc. Moreover, in order to maximize the passenger space in the car, a compact fuel tank of complicated shape is often required. This means that the press formability of the material used is also important. Namely, the material used to fabricate automotive fuel tanks should have the ideal combination

of the properties required in both the fabrication process and the practical use of the tank.

Table 1 shows the materials for automotive fuel tank that were tested in the present study. Both ECOKOTE-S and ECOKOTE-T were given a chromate-free conversion treatment on the Sn-Zn coating layer before they were subjected to the test. As reference materials, TERNESHEET and ALSHEET[®], which have long been applied as steel sheets for automotive fuel tanks were used.⁹⁾

3.1 Exterior corrosion resistance of automotive fuel tanks

In the exterior corrosion resistance test, steel sheets formed into cylindrical cups were used as test samples representing the press forming used in the automotive fuel tank manufacturing process. Although the outer surfaces of fuel tanks are normally painted to improve their resistance to salt corrosion, the corrosion resistance of each of the specimens was evaluated with and without exterior paint in order to clarify the difference made by the coating. The corrosion test was carried out in accordance with JASO-M609-91 (salt water spraying: 2 h → drying: 60°C, 20% RH, 4 h → wetting: 50°C, 95% RH or more, 2 h/cycle).

The unpainted specimens are shown in **Fig. 7** (top). TERNESHEET, which has no sacrificial anticorrosion capability, had specs of red rust on its edge and showed the progression of corrosion. ALSHEET[®] also showed inadequate corrosion resistance. On the other hand, ECOKOTE-T, with the sacrificial anticorrosion capability, showed only slight red rust. ECOKOTE-S showed good corrosion resistance because of the effect of controlling the coating metal layer microstructure and was free from red rust.

The painted specimens are shown in **Fig. 7** (bottom). Like the unpainted specimen of ECOKOTE-S, the painted ECOKOTE-S

shows effective coating metal layer control reflected in the corrosion resistance after painting, suggesting that it should be able to help prolong the service life of automotive fuel tanks.

3.2 Interior corrosion resistance of automotive fuel tanks

As in the exterior corrosion resistance test, cylindrical cups prepared from the steel sheets were used as test specimens in the interior corrosion resistance test. In addition to ordinary gasoline, biodiesel fuel and ethanol-blended gasoline, which are becoming increasingly widespread, were used in the test. To simulate the natural deterioration of fuel while in storage, each of the fuels was subjected to oxidation deterioration before the testing. The conditions of the fuels tested are shown in **Table 2**. Each of the sample fuels was put in a cylindrical cup, which was sealed and held at the prescribed temperature for 1,000 h, to evaluate the interior corrosion resistance.

The steel sheet specimens tested by using the soured gasoline are shown in the top panels of **Fig. 8**. In the test, the fuel separated into two phases, with formic acid and acetic acid being concentrated in the water phase, subjecting the bottom of the cup to severe corrosive conditions. TERNESHEET corroded about 0.2 mm in depth over the surface of the cup that was in contact with the water phase of the fuel. On the other hand, ECOKOTE-T showed less corrosion than TERNESHEET, although a small amount of pitting corrosion was observed at the cup bottom that was in contact with the water phase. ALSHEET[®] and ECOKOTE-S showed still smaller degrees of rust than ECOKOTE-T.

The steel sheet specimens tested by using the soured biodiesel fuel are shown in **Fig. 8** (bottom panels). Since plant-based biodiesel fuel contains double and triple carbon bonds it tends to be oxidized very easily, producing an extremely severe corrosive environ-

Table 1 Automotive fuel tank materials tested in the present work⁹⁾

	Coating layer		Chemical conversion coating
	Composition	Amount of deposition (g/m ² per single side)	
ECOKOTE-S	Sn-7mass%Zn	30	Chromate-free
ECOKOTE-T	Sn-7mass%Zn	30	Chromate-free
TERNESHEET	Pb-8mass%Sn	40	Phosphate treatment
ALSHEET [®]	Al-10mass%Si	40	Chromate-free

Table 2 Fuel conditions in the tests⁹⁾

Fuel used for the test	Content
Soured-gasoline	90vol% soured-gasoline + 10vol% water ; Initial organic acid concentration in the water : acetic acid 100mg/l, formic acid 200mg/l, chloride ion 100mg/l
Soured RME mixture diesel fuel	Soured RME*20 (acetic acid:10ppm) + 10vol% water *RME: rape methyl ester
Soured ethanol	Soured ethanol + 1vol%Water ; Initial organic acid concentration in the fuel : acetic acid 100mg/l, formic acid 200mg/l, chloride ion 100mg/l

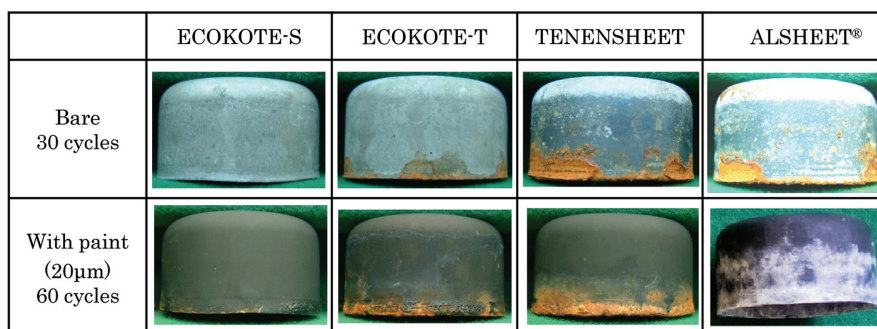


Fig. 7 Result of external corrosion resistance⁹⁾

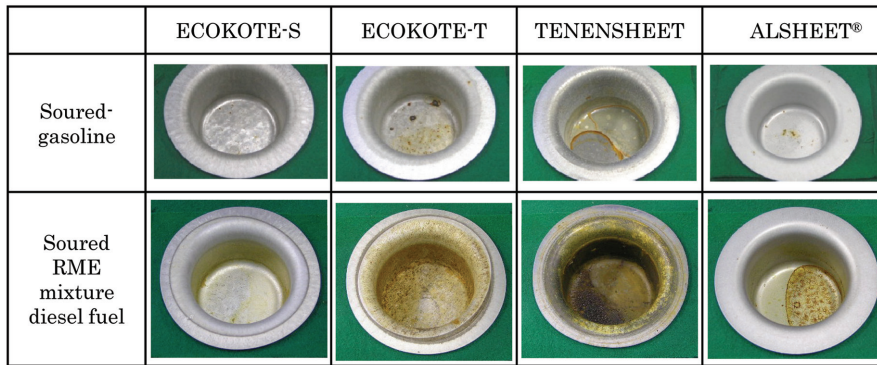


Fig. 8 Result of internal corrosion resistance⁹⁾

ment. Because of this, the reference steel sheets corroded more in the biodiesel fuel than in the soured gasoline. On the other hand, ECOKOTE-S showed good corrosion resistance even in the biodiesel fuel, although it was slightly discolored by the degraded fuel product. This is because Sn, which is the principal component of the coating layer, is relatively stable in the presence of organic acids and the dispersion of fine grains of Zn in the eutectic Sn-Zn helps maintain good corrosion resistance.

As described above, ECOKOTE-S, which has Zn dispersed finely in the eutectic Sn-Zn, has sufficient corrosion resistance and can withstand conventional soured gasoline as well as biodiesel fuels, which are expected to become widespread in the future.

3.3 Production engineering properties required of steel sheets for automotive fuel tank

We studied formability, resistance-weldability, and paintability, which are required of steel sheets used for manufacturing automotive fuel tanks. The study results are described below.

3.3.1 Formability

Fig. 9 shows the limiting drawing ratio of ECOKOTE-S, ECOKOTE-T, TERNESHEET, and ALSHEET®. ECOKOTE-S has good formability comparable to that of ECOKOTE-T and TERNESHEET. In addition, a study of the soundness of each of their coating layers after the processing revealed that the coating layers of ECOKOTE-S, ECOKOTE-T, and TERNESHEET were free from cracking and maintained a good state of surface protection.

3.3.2 Resistance-weldability

Fig. 10 shows the recommended welding current range for spot welding for each of the above steel sheets. ECOKOTE-S is compa-

table to the other steel sheets.

Fig. 11 shows the results of a electrode life test of the various steel sheets. ECOKOTE-S did not pose any practical problems since it demonstrated almost the same electrode life as ECOKOTE-T and ALSHEET®. When compared with TERNESHEET, ECOKOTE-S was far inferior in electrode life. This is because the Cu electrode is easily alloyed with Sn or Zn. On the other hand, we found that the electrode life could be improved by optimizing the welding conditions (pressing force, welding current, heating time, and electrode

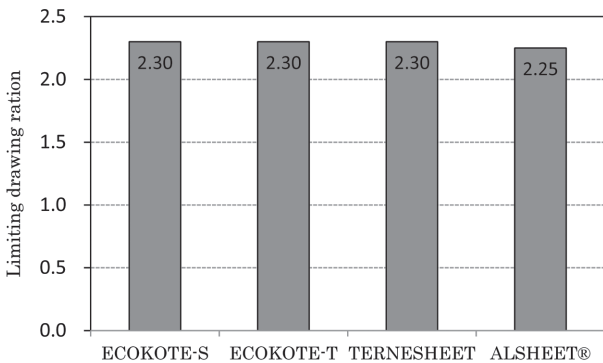


Fig. 9 Limiting drawing ratio⁹⁾

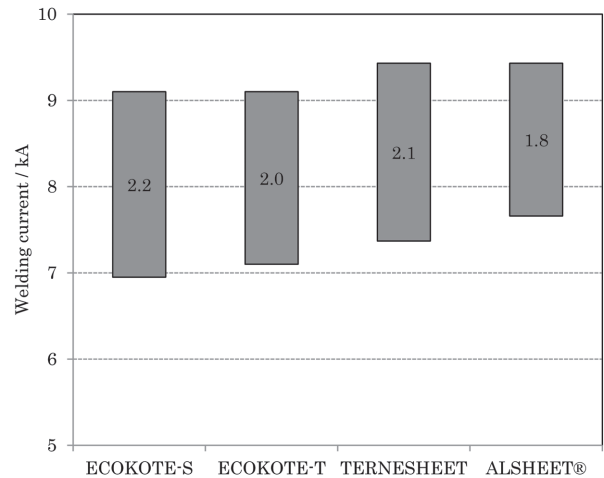


Fig. 10 Available current range for spot welding⁹⁾

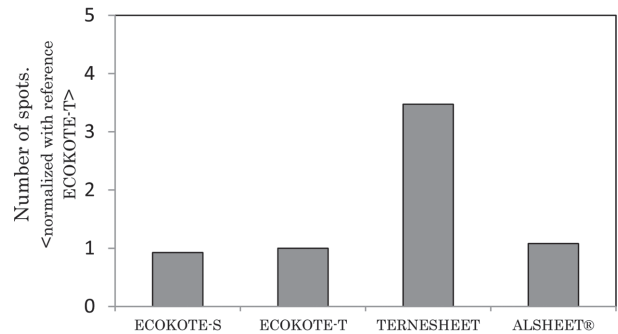


Fig. 11 Continuous spot weldability

Table 3 Performance characteristics of automotive fuel tank materials¹⁰⁾

	External corrosion resistance	Internal corrosion resistance			Formability	Weldability	Paint coating applicability
		Soured-gasoline	Soured bio diesel fuel	Soured ethanol mixture gasoline			
ECOKOTE-S	◎	◎	◎	◎	◎	○	◎
ECOKOTE-T	○	○	△~×	◎	◎	○	◎
ALSHEET®	△	◎	◎	×	△	○	◎
TERNSHEET	△	△	△~×	◎	◎	◎	◎

Note ◎ excellent, ○ good, △ acceptable, × unacceptable

tip shape).

3.3.3 Paintability

We carried out a test to evaluate the paint adhesion for the above steel sheets using typical paints, paint film thicknesses, and baking conditions applied to fuel tanks. The test results showed that all the coated steel sheets were free of blisters or any other surface defects and that the paint film residing ratio after the taping was 100%. This confirmed that the paints and conditions mentioned above could be applied to automotive fuel tanks made from any of the tested steel sheets.

3.3.4 Overall evaluation

Table 3¹⁰⁾ shows the overall performance of each of the above steel sheets for automotive fuel tanks. As described above, ECOKOTE-S was equal or superior to ECOKOTE-T and TERNSHEET in terms of formability, resistance weldability (spot welding, seam welding), and paintability, which are required of steel sheets for automotive fuel tanks.

Our evaluations of the interior and exterior corrosion resistance of automotive fuel tanks described in the previous section confirm that ECOKOTE-S is a steel sheet that can be formed into an automotive fuel tank by using conventional fuel tank manufacturing processes and is compatible with new types of fuels that are expected to become widespread in the future.

4. Conclusions

Our evaluation tests indicated that ECOKOTE-S is a superior recyclable steel sheet that can be used for manufacturing automotive fuel tanks. It can withstand biofuels to help minimize the impact of

fossil fuels on the environment and can be used effectively in an eco-friendly society.

The production of ECOKOTE-S has been expanding ever since it was put on the market in 2005. It is expected that within a few years, ECOKOTE-S will account for a great majority of steel sheets for automotive fuel tanks in Japan. Automakers overseas are also using ECOKOTE-S with positive results.

Acknowledgments

The author wishes to express his heartfelt thanks to Dr. Hisao Esaka, Professor in the Department of Materials Science and Engineering of the National Defense Academy of Japan, for his generous cooperation in the directional solidification test.

References

- Higuchi, S. et al.: Tetsu-to-Hagané. 66 (11), 1016 (1980)
- Nippon Steel Corporation ALSHEET® Catalog
<http://www.nsc.co.jp/product/sheet/pdf/JC134.pdf>
- Maki, J. et al.: Journal of the Surface Finishing Society of Japan. 51 (6), 653 (2000)
- Maki, J. et al.: Materia Japan. 39 (2), 178 (2000)
- Kurosaki, M. et al.: Shinnittetsu Giho. (378), 46 (2003)
- Massalski, T.B. et al.: Binary Alloy Phase Diagrams. 2nd Ed. Ohio, ASM International, 1990, p. 3417
- Izaki, T. et al.: Galvatech 2001. Brussels, 2001, AIM
- Goto, Y. et al.: Journal of the Japan Institute of Metals. 75 (7), 392 (2011)
- Goto, Y. et al.: Zairyo-to-Kankyo. 59 (9), 349 (2010)
- Goto, Y. et al.: Bulletin of the Iron and Steel Institute of Japan. 17 (3), 15 (2012)



Masao KUROSAKI
Chief Researcher, Dr.Eng.
Yawata R&D Lab.
1-1, Tobihata-cho, Tobata-ku, Kitakyushu
Fukuoka 804-8501



Yasuto GOTO
Senior Researcher, Dr.Eng.
Surface Treatment Research Lab.
Steel Research Laboratories



Shinichi YAMAGUCHI
Senior Researcher
Yawata R&D Lab.



Yusho OYAMA
Manager
Sheet & Coil Div.
Yawata Works



Toshinori MIZUGUCHI
Manager
Quality Management Div.
Yawata Works



Teruaki IZAKI
Manager
Automotive Flat Products Sales Div.