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Lightly Tin-Coated Steel Sheet "RIVERWELT" for Welded Cans by Ni-Diffusion Treatment*¹

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1 Introduction

In conventional practices, food and beverage cans were manufactured from heavy-coated tinplates with no lacquering. However, light-coated tinplates with lacquer coating have gradually been adopted, and today they constitute the majority of tinplate cans. Tinfree steel is also used for food and beverage cans because of its excellent lacquer adhesivity and corrosion resistance after lacquering. Since the use of lacquered cans has increased for such reasons, steel sheets for cans are now required to provide excellent lacquer adhesion and corrosion resistance.

Tinplate can body joining was performed by soldering in the past. However, welding has been widely used in place of soldering since the development by Soudronic AG, of a seam welder with an intermediate electrode in copper wire form. Can body joining by welding has the following features:

(1) High can-manufacturing speed

In recent years, the welding speed has reached 50 m/min or more, making it possible to manufacture welded cans at speeds equal to or higher than those of can-making by soldering. Therefore, this joining method is more economical.

(2) Lead-free joining of can bodies

Unlike soldering, welding does not pose the problem of the toxicity of lead; thus, solving the food sanitation problem.

(3) Saving in material

The lap width of jointed can bodies (0.3 to 0.5 mm) is smaller than those obtained by soldering (6.1 mm) and cementing (5 mm). Therefore, material can be saved, making this joining method economical.

(4) Improved appearance

In soldered cans, the area near the joint on the external surface of the can is contaminated with solder. In welded cans, the weld is of good appearance, and excellent printing is possible on the body even near the weld. It is possible to manufacture specially-shaped cans because the weld has high strength and good formability.

In the field of beverage containers, however, there is keen competition between steel cans, glass bottles, paper containers, and aluminum cans. It is, therefore, necessary to improve the performance, quality, and cost competitiveness of steel cans. Although No. 25 tinplate is widely used as material for welded cans, its tin coating can be reduced from the stand-point of weldability for cost saving. Against this background, light-coated steel sheets with good weldability and corrosion resistance

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have been desired as a replacement for No. 25 tinplate. As a result, many types of lightly tin-coated steels (hereinafter called LTS)¹⁻⁹⁾ and nickel-coated steels^{5,10)} were developed, and some have been commercialized.

As a result of research and development efforts, Kawasaki Steel came to manufacture surface treated steel sheets with excellent weldability and corrosion resistance which are suitable for food and beverage cans. The company succeeded in developing a completely new type of LTS "RIVERWELT" using Ni-diffusion treatment. RIVERWELT entered commercial production in April 1984.

This report describes the development policy of RIVERWELT and results of an investigation into the effect of the coating system on quality characteristics.

2 Development Aim

In developing the LTS for welded cans, it was feared that corrosion resistance might decrease if the tin coating weight were simply reduced. Therefore, an attempt was made to compensate for the possible loss in corrosion resistance by improving the electrochemical property of the base steel and alloy layer by use of a method, previously developed by the company, for forming an Ni-diffusion layer on the steel sheet (hereafter called the Ni-diffusion treatment method).¹¹⁾ Furthermore, because the LTS is used after lacquering, it must have excellent lacquer adhesion. Therefore, an attempt was made to apply a special chromate treatment different from the cathodic treatment in a sodium dichromate solution (hereafter called CDC treatment) applied to conventional tinplates.

2.1 Ni-diffusion Treatment Method

The Ni-diffusion treatment is a method¹¹⁾ developed to improve the corrosion resistance of tinplates to can contents with low pH. As an example of experiment, a nickel-plated cold-rolled steel sheet was annealed at 700°C for 30 s to diffuse nickel into the steel sheet. This steel sheet was then electroplated, and flow melting treatment was conducted. Figure 1 shows the effect of the nickel coating weight of this test material on the ATC value (alloy-tin couple current value),¹²⁾ a value which indicates the corrosion resistance to acidic fruits, and the STC value (steel-tin couple current value), which is the couple current value between steel sheet and tin in the ATC test liquid. The ATC and STC values decrease with increasing nickel coating weight, and the electrochemical property of the alloy layer and base steel improves. This decrease in the couple currents between tin (anode) and the alloy coated base steel (cathode) indicates improvement in corrosion resistance. Because the tin coating layer is thin, LTS may cause corrosion problems when lacquer film defects exist. However, a

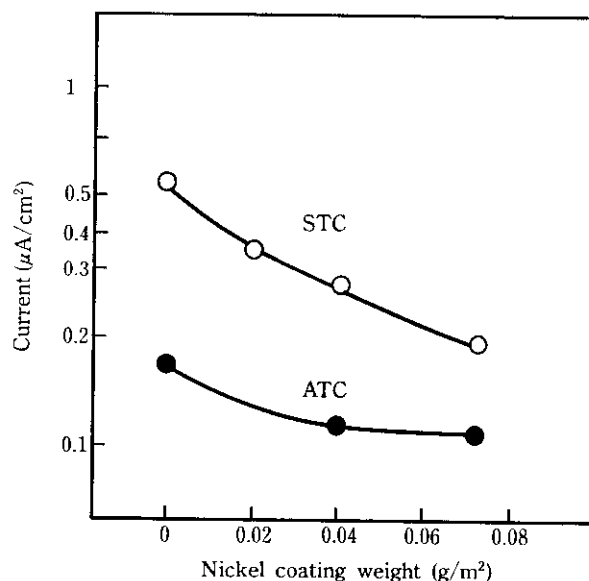


Fig. 1 Effect of nickel coating weight on STC value of Ni-diffusion treated steel and ATC value of Ni-diffusion treated lightly tin-coated steel

satisfactory solution to this problem was anticipated, as it was possible to lower the ATC value and STC value by Ni-diffusion treatment.

2.2 Special Chromate Treatment

Although LTS is internally lacquered before use, it is desirable that the lacquer adhesion be high from the standpoint of corrosion resistance because of the thinness of the coating film. The film on tinfree steel sheet is composed of metallic chromium and hydrated chromium oxide. This steel is excellent in lacquer adhesion and also provides excellent corrosion resistance, even with very thin films. On the other hand, in the conventional, CDC-treated tinplate, the surface film is a chromate film comprising almost entirely hydrated chromium oxide, and the lacquer adhesion is not necessarily high. Therefore, lacquer adhesion was improved by conducting special chromate treatment to form a surface film composed of metallic chromium and hydrated chromium oxide.

3 Experiment Method

3.1 Production of Test Materials

The manufacturing process for RIVERWELT is shown in Fig. 2. After electrocleaning in the continuous annealing line (CAL), a cold-rolled steel sheet was electroplated with nickel and annealed at 700°C for 30 s in an HN gas (7% H₂ + 93% N₂) to form an Ni-diffusion layer on the steel. After ordinary temper rolling, the steel sheet was subjected to electrocleaning, sulfuric acid

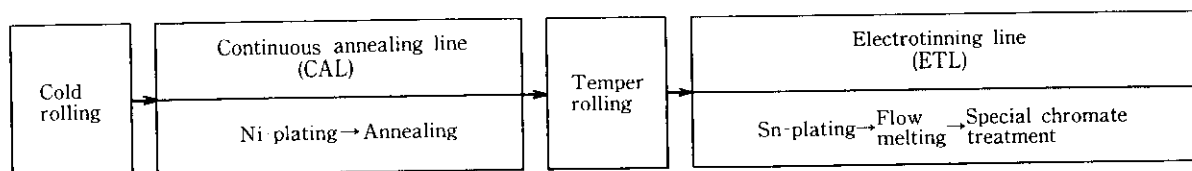


Fig. 2 Manufacturing process of Ni-diffusion treated lightly tin-coated steel "RIVERWELT"

pickling, and tin-plating in a halogen bath in the electroplating line (hereafter called ETL). Subsequently, also in the ETL, tin was melted to obtain an alloy layer of 0.2 to 0.3 g/m². After that, a special chromate film was formed by cathodic electrodeposition in a low-concentration aqueous solution of chromic acid.

3.2 Methods of Measuring Coating Weights

The following methods of measuring coating weights were used:

- (1) Nickel coating weight: Fluorescent X-ray method
- (2) Tin coating weight:
 - Total tin weight—Chemical analysis or fluorescent X-ray method
 - Metallic tin weight—Coulometric method (2 mA/cm² current is anodically applied in 1.0 M HCl.)
 - Alloyed tin weight—Total tin weight minus metallic tin weight
- (3) Chromium coating weight:
 - Total chromium weight—Fluorescent X-ray method
 - Metallic chromium weight—Coulometric method (25 μ A/cm² current is anodically applied in a pH 7.4 buffer solution of phosphate.)
 - Hydrated chromium oxide weight—Total chromium weight minus metallic chromium weight

3.3 Contact Resistance

The test material was baked under conditions equal to those of actual lacquering and print-baking, i.e., at 210°C for 20 min. The contact resistance of the test material was measured using an SQ meter⁽¹³⁾ (surface quality meter).

3.4 Welding Test

The test material was baked at 210°C for 20 min prior to the welding test conducted under the following conditions, using an electric resistance welder with an intermediate electrode in copper wire form.

- (1) Welder
FX400 (manufactured by Fuji Kogyosho Co., Ltd.)
- (2) Welding conditions
 - Overlap : 0.3 to 0.5 mm
 - Welding speed : 40 m/min
 - Welding force : 40 kg

The weld strength was examined by the peel test, in which a cut is made into an edge of the weld and the weld is peeled from the can body. Weldability was

evaluated in the available welding current range where the weld strength is adequate and no splash is found.

3.5 Rust Resistance Test

Test specimens without lacquer were held for 96 h in a test vessel under the following alternating dry and wet conditions:

Dry condition Temperature: 25°C Relative humidity: 50%	\longleftrightarrow Alternated every 30 min	Wet condition Temperature: 50°C Relative humidity: 98%
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3.6 Lacquer Adhesion Test

A 50 mg/dm² epoxy-phenolic coating was applied to two specimens (5 × 100 mm²). The parts of the specimens corresponding to a 90-mm length from the end were cemented with nylon adhesive while being heated, and the unbonded part was bent outward. The lacquer adhesion was evaluated in the T-peel test by peeling off the cemented part of the T-shaped specimen at a tension speed of 200 mm/min and measuring the tensile strength.

3.7 Tests of Corrosion Resistance after Lacquering

The following tests were conducted on specimens to which a 50 mg/dm² epoxy-phenolic coating had been applied:

- (1) Undercutting corrosion (UCC) test⁽¹⁴⁾

Cross cuts were made into the coating film of the specimen. It was then immersed in 1 : 1 mixture of an aqueous solution of 1.5% citric acid and a solution of 1.5% salt. After holding at 25°C for 96 h, the width of the film delaminating from the crosscut portions was measured.

- (2) Blister resistance test

The lower half of a specimen (40 × 80 mm²) was immersed in boiled commercial tomato juice and, after being sealed, was held at 55°C for 18 days. Blistering of immersed and nonimmersed portions was compared.

3.8 Sulfuric Stain Resistance Test

A specimen was bulged 5 mm using the Erichsen testing machine. The specimen was then immersed in a test solution of 1% Na₂S with a pH adjusted to 7 by lactic acid (pH 3.5) and, after heating, held at 110°C for

60 min. Sulfide blackening of the bulged and nonbulged portions was observed.

4 Results and Discussion

4.1 Film Structure

Results obtained with various analysis devices suggest that the LTS coating film, as illustrated in Fig. 3 is composed of an Ni-diffusion layer (Fe-Ni alloy) formed from the base metal by continuous annealing, an Fe(Ni)-Sn alloy layer formed by flow melting treatment, a metallic tin layer, and a special chromate layer consisting of metallic chromium and hydrated chromium oxide to the exposed surface.

Nickel distribution in the depth direction before and after the continuous annealing of a nickel-plated steel sheet was measured by the glow discharge spectrometry (GDS), with the results shown in Fig. 4. It can be seen that nickel has alloyed with the steel sheet during annealing.

An X-ray diffraction revealed that the Fe(Ni)-Sn alloy layer formed by flow melting treatment after tinplating has the same diffraction pattern as FeSn_2 . A sample of this alloy layer, with a nickel coating weight of 0.07 g/m^2 , was taken and subjected to chemical analysis. The results are as follows:

Fe: 14.4 wt%

Ni: 3.5 wt%

Sn: 82.1 wt%

Since the Fe : Sn ratio of FeSn_2 alloy of ordinary tinplate is 18.8 wt% : 81.2 wt%, and with the Fe(Ni)-Sn alloy the ratio is 17.9 : 82.1, it is supposed that in the case of Ni-diffusion, some Fe lattice points of FeSn_2 are replaced by Ni. Thus the concentrations of these atoms show good agreements within the limits of analytical errors.

The base metal was analyzed by IMMA after continuous annealing. The highest concentration of Ni was

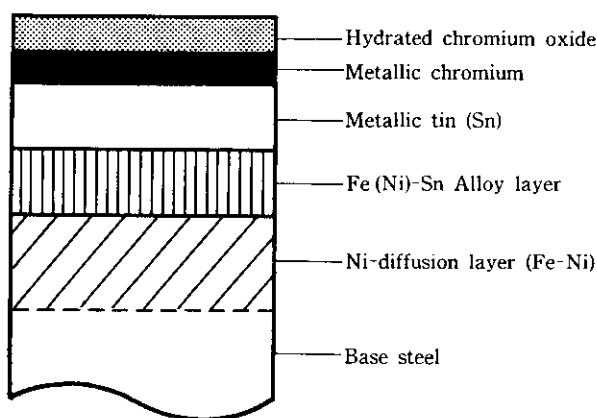


Fig. 3 Schematic cross section diagram of RIVER-WELT

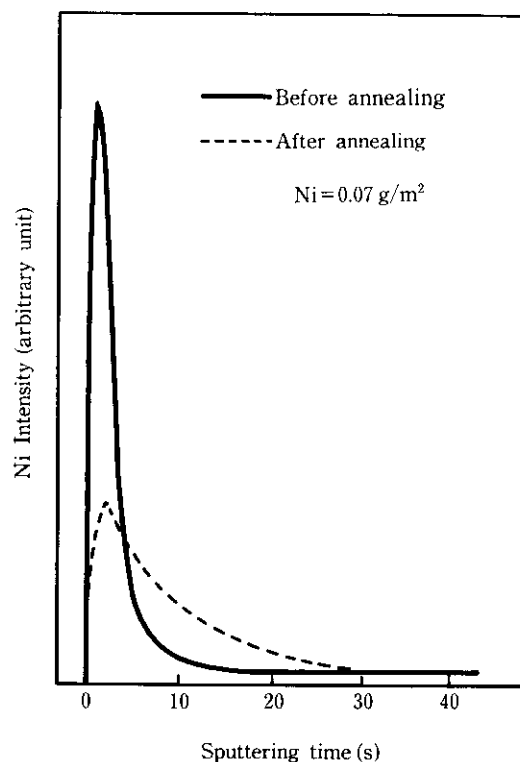
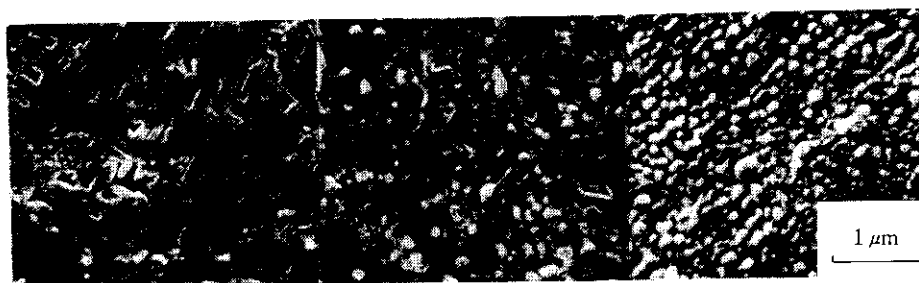


Fig. 4 Glow discharge spectrometric (GDS) depth analysis of Ni-plated steel sheet before and after the continuous annealing process

about 20 wt% and its location was at about 100 \AA depth from the surface. This value agrees well with the ratio of Ni content to the sum of Fe and Ni contents of the Fe(Ni)-Sn alloy layer separated from the base metal. This suggests that the Fe and Ni atoms which constitute the Fe(Ni)-Sn alloy layer during the flow melting treatment nonselectively form an Fe(Ni)-Sn alloy layer of CuAl_2 type.¹⁵⁾ Incidentally, the amount of the base metal that alloys with tin is 60 to 90 \AA in thickness. This is because the amount of tin which alloys during the flow melting treatment is controlled to 0.2 to 0.3 g/m^2 . It seems that the Ni content at about 100 \AA depths from the surface affects the form of the alloy layer, which will be described later.

After dissolution of metallic tin, the Fe(Ni)-Sn alloy layer was removed with nital from the base metal and observed from the base metal side by use of a scanning electron microscope. Photo 1 shows scanning electron micrographs. A conventional alloy layer does not cover the entire steel sheet because it is composed of characteristic prismatic crystals with numerous gaps. The alloy layer formed on a steel sheet subjected to Ni-diffusion, however, is composed of granular crystals, is homogeneous and very continuous, and has few gaps. Under the annealing conditions used in the experiment, gaps exist in areas of the alloy layer at a nickel coating weight of



(a) Fe-Sn

(b) Fe(Ni)-Sn
Ni=0.02 g/m²

(c) Fe(Ni)-Sn
Ni=0.07 g/m²

Photo 1 Scanning electron microphotographs of Fe-Sn and Fe(Ni)-Sn alloy layer (stripped side surface) at the interface of the alloy layer and the base steel

0.02 g/m². The alloy, however, is completely continuous, with no gaps, when the nickel coating weight is above 0.04 g/m². It is thought that the nickel in the Ni-diffusion layer on the steel sheet assists the nucleation of the Fe(Ni)-Sn alloy layer and contributes to the formation of a dense alloy layer. The reason that gaps are observed in the alloy layer at a nickel coating weight of 0.02 g/m² seems to be that the coating of the steel sheet by nickel-plating is nonuniform, and portions where the nickel concentration is insufficient exist on the surface even after the diffusion treatment.

4.2 Weldability

The side seam of the can body must have high strength and, at the same time, be free of splashes. The weldability of steel sheets is evaluated by the available welding current range within which these requisites can be satisfied. Incidentally, it is well known that there is a good correlation between weldability and the contact resistance of a coating film and that weldability declines as contact resistance increases.¹⁶⁾ Therefore, test specimens of different contact resistance were prepared by varying the tin coating weight and the total chromium coating weight. The available welding current range for these specimens was then investigated. As shown in Fig. 5, it was found that a satisfactory welding current range exists when the contact resistance measured by an SQ meter is 2 Ω or less.

It was expected that contact resistance would be greatly affected by the amount of chromate film, since chromate film has poor electric conductivity, and by the weight of metallic tin, because metallic tin permits soft, good contact with the steel sheet. Therefore, an investigation was made into the effects on contact resistance of the total chromium coating weight (the ratio of the metallic chromium weight to the chromium oxide weight being about 1 : 1) and the metallic tin weight. In this case, the steel sheets were baked at 210°C for 20 min to simulate lacquer baking. The results are shown in Fig. 6. The effect of the metallic tin weight on contact resist-

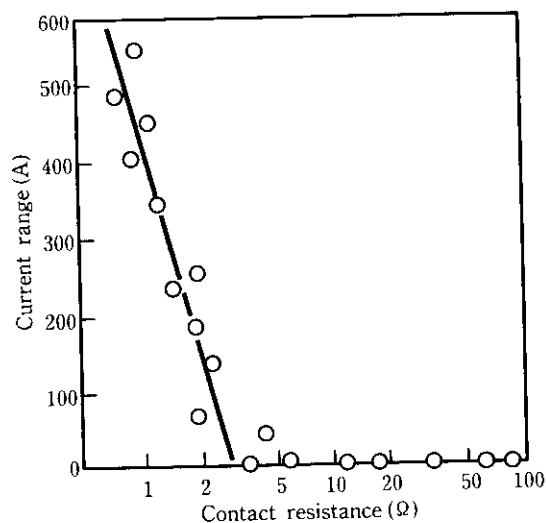


Fig. 5 Relationship between contact resistance and available welding current range at the welding speed of 40 m/min

ance is greater than that of the total chromium coating weight. In the total chromium weight range of 20 mg/m² or below, the contact resistance is 2 Ω or less if 0.1 g/m² or more metallic tin remains after baking.

It was found that the metallic tin weight has a great effect on contact resistance, and therefore, on weldability. As a result, alloying of tin during lacquer baking was studied including the effect of nickel coating weight and total chromium coating weight on after-baking metallic tin weight. **Figure 7** shows the effects of nickel coating weight and flow melting treatment on alloying in the case of No. 7 tinplate. When the flow melting treatment is not conducted, the rate of alloying in the baking process at nickel coating weights of 0.04 g/m² or more is noticeable; it is impossible to leave 0.1 g/m² or more metallic tin. Also, even when the flow melting treatment is performed, the rate of alloying is noticeable if the nickel coating weight exceeds 0.1 g/m². With respect to

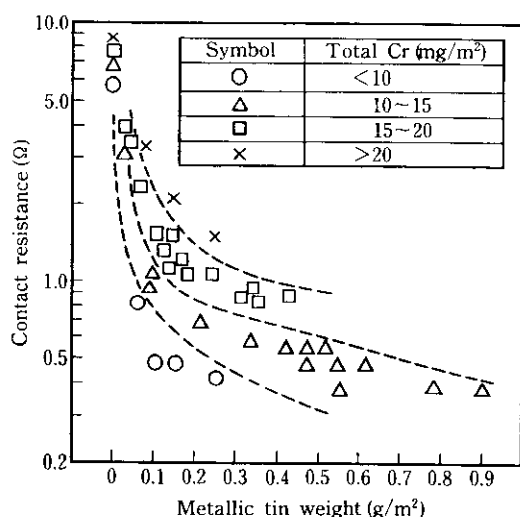


Fig. 6 Effects of metallic tin and total chromium coating weight on contact resistance (by SQ meter) after baking at 210°C for 20 min

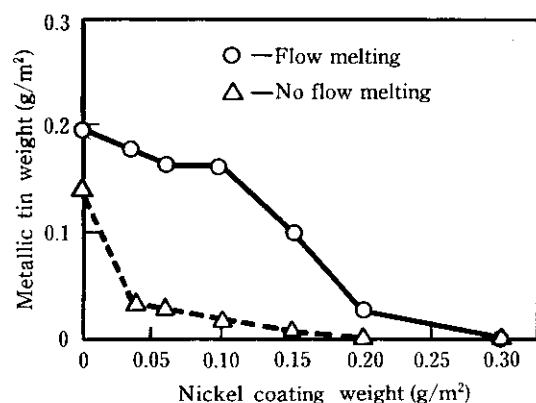


Fig. 7 Effects of Ni-coating weight and flow melting on residual metallic tin weight after baking at 210°C for 20 min

the nickel coating weight, therefore, the lower limit necessary for making a dense Fe(Ni)-Sn alloy layer without the gaps described above was determined to be 0.04 g/m², and the upper limit necessary for leaving 0.1 g/m² or more metallic tin after lacquer baking, was 0.1 g/m². Analysis of the Ni-diffusion layer in the base metal by IMMA indicated that the maximum nickel concentration at about a 100 Å depth from the surface is 5 to 30 wt% for nickel coating weights of 0.04 to 0.1 g/m², depending on the coating weight. It is necessary, therefore, to control the nickel coating weight so that the surface nickel concentration can be within this range even when changes in continuous annealing conditions are required.

When tin-plating is conducted without the diffusion treatment after nickel-plating, Ni and Sn form an alloy at room temperature, as shown in Fig. 8. The weight of the

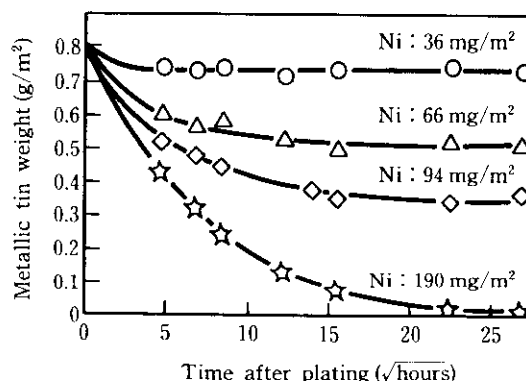


Fig. 8 Decrease in metallic tin weight by Ni-Sn alloying at room temperature on the lightly tin-coated steel which was produced by initial Ni coating and tin coating (0.78 g/m²) followed by chemical treatment process

Ni-Sn alloy is proportional to the nickel coating weight. However, this alloying at room temperature does not take place in Ni-diffusion treated steel sheets.

Even with the Ni-diffusion treatment, lacquer baking causes tin alloying unless flow melting treatment is carried out after tin-plating. It is essential to conduct flow melting because the dense alloy layer formed by this treatment delays the alloying of tin during the subsequent lacquer baking process.

As mentioned above, 0.1 g/m² or more metallic tin remains in No. 7 tinplate after lacquer baking when the nickel coating weight is properly controlled within the 0.04 to 0.10 g/m² range and flow melting is performed. As a result, such No. 7 tinplate has low contact resistance and excellent weldability.

Accordingly, further investigations were deemed necessary only in the case of No. 7 tinplate, and its lacquer adhesive properties and corrosion resistance were studied.

4.3 Rust Resistance

The construction of the coating film of LTS produced by the Ni-diffusion method is effective in suppressing the dissolution of tin because of the strong cathodic polarization of the base steel and alloy layer in deaerated acidic juice, as mentioned above. It is said, however, that tin usually acts as cathode and the base steel as anode in an aerated neutral condition, such as in air. It was unclear whether a similar effect would obtain if the electrochemical property of the alloy were changed. To investigate the electrochemical behavior of coating films during atmospheric corrosion, the corrosion potentials of tin, nickel, an ordinary steel sheet, and an Ni-diffusion treated steel sheet were measured in an aerated 3% NaCl solution. The results are shown in Fig. 9. The ordinary steel sheet is about 130 mV less noble than tin and this

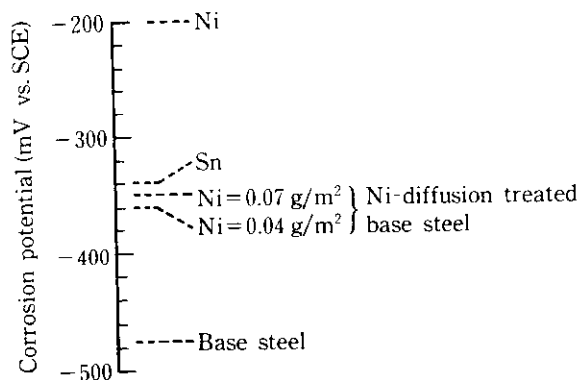


Fig. 9 Corrosion potentials of pure Ni, pure Sn, Ni-diffusion treated base steels, and base steel in aerated 3% NaCl solution

relationship of corrosion potentials is opposite to that observed in a deaerated acidic juice. Therefore, the steel sheet acts as an anode when a corrosion cell is made from the steel sheet and tin, promoted the dissolution of the steel. The Ni-diffusion treatment causes the corrosion potential of the steel sheet to increase and approach the potential of tin. The potential difference between the steel sheet and tin decreases to about 10 mV. It follows that galvanic corrosion in the air is unlikely. As the corrosion potential of nickel is 140 mV noble than that of tin, the diffusion of nickel into the steel sheet alters the potential of the steel sheet favorably in terms of the atmospheric corrosion.

The results of the dry and wet cycle test on the Ni-diffusion treated LTS are shown in **Fig. 10**. It was found that rust resistance is significantly improved by Ni-diffusion and that Ni-diffusion treated No. 7 tinplate has sufficient rust resistance at chromium coating weights of 5 mg/m² or more, at least equal to that of No. 25 tinplate.

4.4 Lacquer Adhesion

Table 1 gives the T-peel strength of No. 25 tinplate, Ni-diffusion treated LTS subjected to the cathodic dichromate treatment, RIVERWELT, and tinfree steel. The lacquer adhesion of No. 25 tinplate is lower than those of other steel sheets. Ohyama et al.¹⁷⁾ have reported that the lacquer peeling of tinplate occurs at the interface between tin and tin oxide or in the tin oxide film, and that the weak adhesion is due to low strength of these regions. The lacquer adhesion of CDC-treated LTS is slightly stronger than that of No. 25 tinplate. Kuroda et al.¹⁾ have reported that fragile tin oxides do not readily form on the Fe-Sn alloy layer which explains the excellent lacquer adhesion of Fe-Sn alloy. Since the LTS surface has a thin coating film, the alloy layer is sometimes partially exposed; this seems to account for its somewhat high lacquer adhesion force. RIVERWELT shows very strong lacquer adhesion due to the

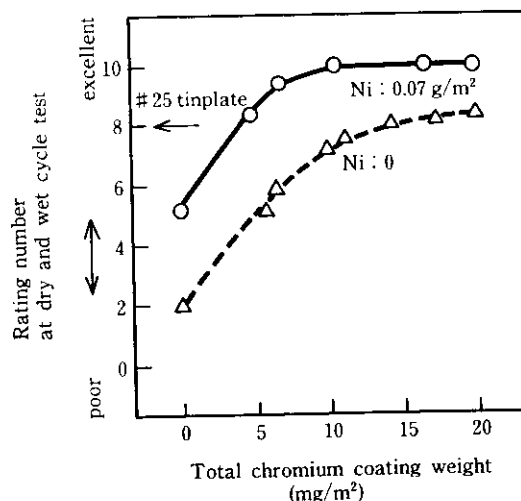


Fig. 10 Effects of Ni-diffusion treatment and total chromium coating weight on dry and wet cycle corrosion resistance of lightly tin-coated steel with tin coating weight of 0.78 g/m²

Table 1 T-peel strength of the various coated steels for cans

Sample	T-peel strength (kg/5 mm)
# 25 Tinplate	0.05
Ni-diffusion treated LTS* with conventional chromate film	0.63
RIVERWELT	3.05
Tin free steel	6.75

* LTS; Lightly tin coated steel

effect of the special chromate treatment. Takano et al.¹⁸⁾ applied cathodic treatment to a tinplate in a CrO₃/SO₄²⁻/F⁻ solution to form metallic chromium plus hydrated chromium oxide. According to their report on this tinplate, peeling occurs at the interface between the chromium and chromium oxide, and the lacquer adhesion force is very high. The surface of tinplate on which metallic chromium is deposited has a lamellar structure of tin/chromium/chromium oxide and metallic chromium is bonded directly to metallic tin without the forming of an intermediate fragile tin oxide layer. This seems to account for its strong lacquer adhesion.

4.5 Corrosion Resistance after Lacquering

The UCC test and blister resistance test were conducted as tests for corrosion resistance after lacquering to investigate the corrosion resistance to can contents.

Figure 11 shows the effect of the metallic coating weight of the special chromate film on the delamination

width of lacquer film in the UCC test. In this figure, the coating films with a metallic chromium coating weight of zero are composed only of hydrated chromium oxides, which are produced by the CDC treatment method. It is apparent from this figure that Ni-diffusion treatment is effective in reducing the delamination width of lacquer film. This effect seems to be explained by the same mechanism as that by which Ni-diffusion promotes a decrease in the ATC value. That is to say, the tin in cross cut portions acts as an anode to the alloy layer or base metal because the test solution has a low pH of 2.1 and is deaerated. However, the dissolution of tin decreases because the cathodic polarization of the base metal and alloy layer is promoted by Ni-diffusion.

An increase in the metallic chromium coating weight also results in a marked decrease in the delamination width. This should be explained by improvement of lacquer adhesion as mentioned above.

Underfilm corrosion may take place, with a stain-like discolored area forming inside the can at the head space, if deaeration is insufficient and the partial pressure of oxygen gas is high when cans are actually filled. Therefore, a blister resistance test was devised to investigate resistance to this type of corrosion. Test specimens with different metallic chromium coating weights and total chromium coating weights were made by altering the conditions of the special as well as the conventional chromate treatment for Ni-diffusion treated No. 7 tinplate. Results of the test on these specimens are shown in Fig. 12. It can be seen from these results that blistering depends on the metallic chromium coating weight, and not on the total chromium coating weight and that no blisters are produced when the metallic chromium coating weight is 3 mg/m² or more. Therefore, to prevent blistering, the metallic chromium coating weight must be 3 mg/m² or more.

In this study blistering occurred mainly on the gas phase side near the gas-liquid interface, as it does in actual cans. The pH of the aqueous solution contained in blisters was 10 or more, which means that this portion acts as a cathode in the corrosion reaction. Two possible explanations of the corrosion mechanism have been advanced. On the one hand, an H₂O film may form in a portion of poor lacquer adhesion, and osmotic pressure increase due to the dissolution of soluble substances in this H₂O, with the resulting entry of H₂O from outside causing the coating film to peel off.¹⁹⁾ Alternatively, it may be said that the oxygen reduction reaction results in the formation of alkalis, which in turn raises pH, resulting in deterioration of the coating film and the loss of bonding strength between the coating film and the steel sheet, causing the coating film to peel off.²⁰⁾ This delamination, in any case, allows corrosion to begin and spread.

The effectiveness of the special chromate treatment in preventing corrosion is attributable to the fact that, as

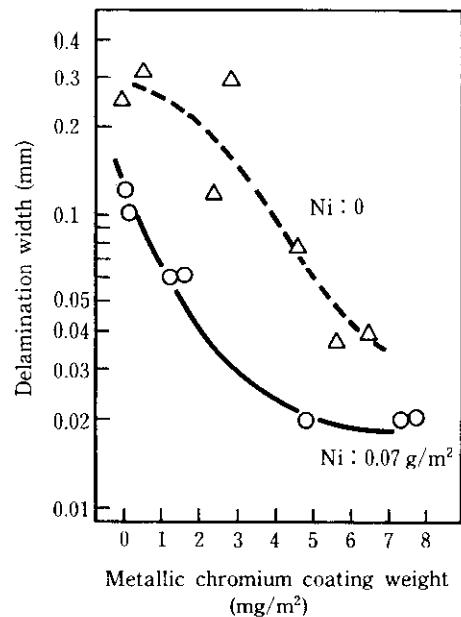


Fig. 11 Effects of Ni-diffusion treatment and metallic chromium coating weight on delamination width of lacquer after undercutting corrosion test for 96 h

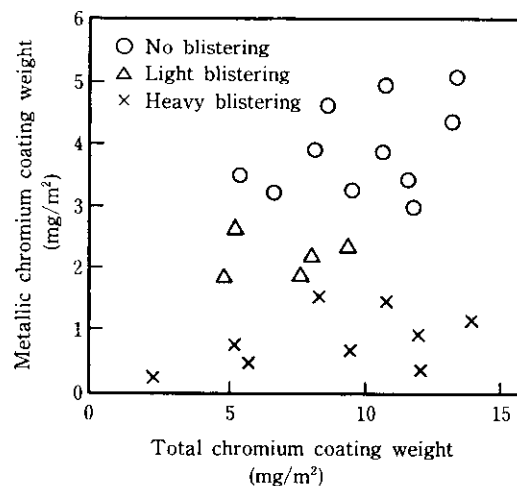


Fig. 12 Effects of metallic chromium and total chromium coating weight on blister formation in deaerated tomato juice at 55°C for 18 days

mentioned above, H₂O films do not readily form due to good lacquer adhesion, and to the fact that the existence of both metallic chromium and hydrated chromium oxide inhibits the cathodic reaction on the surface. As pointed out by Okada et al.,²¹⁾ metallic chromium is very effective in inhibiting the hydrogen evolution reaction, while the hydrated chromium oxide in the top layer inhibits the oxygen reduction reaction.

4.6 Sulfide Stain Resistance

When tinplates are used for fish cans, sulfur-containing amino acids in the food may thermally decompose in the high-temperature pasteurization process, forming SnS, and resulting in sulfide staining. However, the sulfide staining resistance of RIVERWELT in both bulged and nonbulged parts is by far superior to that of No. 25 tinplate and equivalent to that of tinfree steel. Sulfide staining can be reduced by the CDC treatment or special lacquering.²²⁾ Rocquet et al.²³⁾ have reported that metallic chromium deposited by the chromate treatment is especially effective for this purpose. The excellent sulfide stain resistance of RIVERWELT seems to result from the metallic chromium content of its special chromate film.

5 Conclusions

Kawasaki Steel has developed "RIVERWELT," a new, lightly tin-coated steel sheet for welded cans, using the Ni-diffusion method. In the production process, a nickel-plated steel sheet is continuously annealed to form an Ni-diffusion layer. This base metal is plated with tin and partially flow-melted to cause partial alloying of the tin. Finally, a special chromate film is formed on the sheet.

RIVERWELT has the following features:

- (1) The Fe(Ni)-Sn alloy layer formed by flow melting delays the alloying of tin with the base metal during lacquer baking, allowing metallic tin to remain in amounts of 0.1 g/m² or more. Therefore, excellent welds can be obtained even by high-speed welding at welding speeds of 40 m/min or more.
- (2) Couple currents of the Ni-diffusion treated steel sheet and tin in a deaerated acidic fruit juice are small, and the difference in corrosion potential between the Ni-diffusion treated steel sheet and tin in a neutral aqueous solution, a simulated atmospheric condition, is also small. Therefore, the RIVERWELT surface is resistant to corrosion.
- (3) The Fe(Ni)-Sn alloy layer formed on Ni-diffusion treated steel is dense and highly continuous and provides good coverage for the base metal. Therefore, this layer improves corrosion resistance.
- (4) The special chromate film composed of metallic chromium and hydrated chromium oxide improves lacquer adhesion and is very effective in inhibiting

under film corrosion.

- (5) RIVERWELT matches No. 25 tinplates in corrosion resistance when lacquered or in the atmosphere without lacquer.

References

- 1) H. Kuroda, I. Onoda, T. Inui and Y. Kondo: "Characteristics of Lightly Tin-coated Steel Sheet", *Proceedings of Second International Tinplate Conference*, ITRI, London, 124-135
- 2) R. Allouf and C. Mergey: "A New Light Tin-Coated Steel for Can-making", *Proceedings of Second International Tinplate Conference*, ITRI, London, (1980), 241-251
- 3) J. P. Servais, J. Lempereur, L. Renard and V. Leroy: *ATP, Centre Nationale de Recherches Metallurgique*, **56**(1980), 43-52
- 4) *Tin International*, **54**(1981)12, 490
- 5) H. Asano, S. Higuchi and M. Higashi: *The Journal of the Metal Finishing Society of Japan*, **33**(1982)10, 509-515
- 6) K. Mochizuki, H. Nakakouji, J. Kokubu, Y. Sakamoto, T. Ichida and T. Irie: *Tetsu-to-Hagané*, **69**(1983)13, S1231
- 7) H. Nakakouji, K. Mochizuki, J. Kokubu, Y. Sakamoto, T. Ichida, T. Irie: *Tetsu-to-Hagané*, **69**(1983)13, S1232
- 8) H. Nakakouji, H. Ogata, K. Mochizuki, T. Ichida, T. Irie: *Tetsu-to-Hagané*, **70**(1984)5, S326
- 9) Y. Yomura, H. Kagechika, H. Takano, T. Hara: *Tetsu-to-Hagané*, **70**(1984)5, S322
- 10) *Modern Metals*, **36**(1980)9, 86-94
- 11) Kawasaki Steel Corp.: Japan Patent Application No. 54-20940
- 12) G. G. Kamm, A. R. Willey, R. E. Beese and J. L. Krickl: *Corrosion*, **17**(1961)2, 106-114
- 13) M. Matsunaga: "Hyomen-Sokutei - Kogyo-gijutsu-Zensho 22," 93-109
- 14) O. D. Gonzalez, P.H. Josephic and R. A. Oriani: *J. Electrochem. Soc.*, **121**(1974)1, 29-34
- 15) R. W. G. Wyckoff: "Crystal Structures", vol. 1, (1963), [John Wiley & Sons]
- 16) M. Sodeik: "Influences of Material Properties on Side Seam Welding of Cans made of Tinplate", *Proceedings of Second International Tinplate Conference*, ITRI, London, (1980), 161-175
- 17) T. Oyama, A. Miyachi, T. Nemoto and K. Yamada: *Technical Reports of Toyō Kōhan Company Ltd.*, **16**(1967)1, 2, 56-76
- 18) H. Takano and T. Watanabe: "Effect of Passivation Treatment on Lacquer Adhesion of Tinplate", *Proceedings of Second International Tinplate Conference*, ITRI, London, (1980), 422-433
- 19) D. M. Brasher and T. J. Nurse: *J. Appl. Chem.*, **9**(1959), 96
- 20) J. S. Hammond, J. W. Holubka, J. E. Devries and R. A. Dickie: *Corros. Sci.*, **21**(1981)3, 239-253
- 21) H. Okada and H. Matsuda: *Boshoku Gijutsu* (Corrosion Engineering), **19**(1970)1, 2-10
- 22) T. Inui, T. Nemoto, K. Saijo and H. Kawamura: *Tetsu-to-Hagané*, **68**(1982)7, 850-857
- 23) P. Rocquet and P. Aubrun: *Br. Corros. J.*, **5** Sept. (1970), 193-197