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Pb Free Zn-Sn-Ni Alloy Coated Steel Sheet for Electric Devices

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Abstract

Environmental problems in recent years are increasing the demand for freedom from lead. Nippon Steel developed Zn-Sn-Ni alloy coated steel sheets that improve on the corrosion resistance and whisker formation of electrolytic tinplate traditionally used as coated steel for electronic parts. The zinc, tin, and nickel are sequentially applied to steel strips on an electrolytic tinning line and are subjected to a thermal diffusion alloying treatment by a reflow unit to form a Zn-Sn-Ni alloy mainly composed of Sn and Zn. The Zn-Sn-Ni alloy coated steel sheet features excellent corrosion resistance, solderability and whisker resistance as coated steel sheets for electronic parts.

1. Introduction

Environmental problems in recent years have called the toxicity of lead into question and are increasing the demand for freedom from lead. The household electric appliance industry has developed Sn-Ag and Sn-Bi alloys as substitutes for Sn-Pb solder and it is now studying their production application[1,2].

Lead-coated steel sheets (terne sheet) are used in large amounts as coated steel for electronic parts. Terne sheet is press formed and joined with Sn-Pb solder in many cases. Most of the coatings applied to steel sheets for electronic parts contain lead. Electrolytic tinplate is used in some applications, but the number of electronic parts in which electrolytic tinplate is used is limited by the lack of corrosion resistance and the formation of needle-like single-crystal tin whiskers that cause short-circuit faults.

The authors studied the method composed of multiple-layer coating and thermal diffusion as means for improving the above-mentioned two shortcomings by alloying tin with other metals and utilizing a thermal diffusion process[3]. As a result of the study, the authors succeeded in developing and commercializing a Zn-Sn-Ni alloy-coated steel sheet that solves the above-mentioned problems of terne sheet (tinplate). The new coated steel is produced by a process consisting of sequentially depositing the nickel, tin and zinc on steel a strip, and heating the coated strip with a tin melting unit on an electrolytic tinning line to diffuse and alloy the nickel, tin and zinc layers.

This report describes the behavior of the three deposited metals layers during thermal diffusion, the structure of the formed coating, and the corrosion resistance, solderability, whisker formation and other service performance properties of the coated product.

2. Experimental Methods

2.1 Materials

The Zn-Sn-Ni alloy-coated steel sheet was manufactured by sequentially depositing the nickel, tin and zinc on 0.4-mm thick steel strip on an electrolytic tinning line, and heating the coated strip with a tin melting unit to cause the thermal diffusion and alloying of the three metal layers. The zinc, tin and nickel coating weights depend on the parts (solder wettability) to be fabricated from the coated sheet. As control materials, #50 tinplate and terne sheet of the same thickness were used. **Table 1** lists the coating weights of these coated steel sheets.

2.2 Heat treating conditions

The tin melting unit of the electrolytic tinning line was used for the heat treatment. The heating temperature and speed were controlled by adjusting the strip speed and voltage. The coated strip was heated under atmospheric pressure. After the heating operation, the

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Table 1 Coated steel sheets

	Coating weight (g/m^2)			
	Zn	Sn	Ni	Pb
Zn-Sn-Ni	0.1 - 0.4	4.0 - 5.6	0.1 - 0.4	—
#50 tinplate	—	5.6	—	—
Terne sheet	—	3.0 - 4.0	—	36 - 48

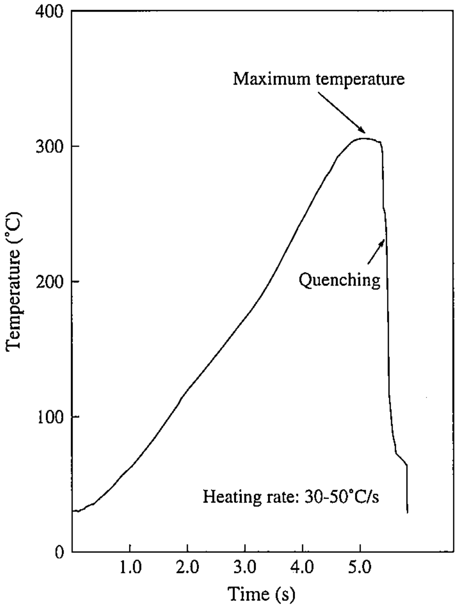


Fig. 1 Typical heat pattern for thermal diffusion alloying

strip was immediately cooled in water at a temperature of 30 to 40°C. The terms "heating time" and "heating temperature" used in this report refer to the time for the strip to reach the maximum possible temperature from room temperature and the maximum possible temperature of the strip, respectively. That is, a heating temperature of 300°C and heating time of 5 s mean that the maximum possible heating temperature and the time taken to reach 300°C are 300°C and 5 s, respectively. **Fig. 1** shows a typical heating pattern.

2.3 Measurement of natural electrode potential and polarization curve

The natural electrode potential and polarization curve were measured on a 20 × 20 mm area on each 25 × 25 mm specimen whose top and bottom surfaces were sealed with propolis. A Hokuto Denko constant-current and constant-voltage generator was used for taking the measurements.

2.4 Analysis of thermal diffusion alloy layers

The thermal diffusion Zn-Sn-Ni alloy coating was analyzed by such instruments as an Analymat Model 2504 glow discharge spectrometer (GDS) and a Rint Model 1000 X-ray diffractometer (copper target, cobalt filter, 40 kV, 250 mA). The coating weight of each metal was determined by a Rigaku Denki X-ray fluorescence analyzer using prepared calibration curves.

2.5 Corrosion resistance

Salt spray test (SST)

To evaluate their salt spray corrosion resistance, prepared specimens were sprayed with the JIS-specified 35°C, 5% salt solution for 72 h, and their rusted areas were then measured.

2.6 Solderability

(1) Solder wettability

For solder wettability, the wetting start time (zero cross time) was measured by a Rhesca Model SAT-2000 solder checker. The H63A solder specified in JIS Z 3282 was used, and Sn-3.5%Ag and Sn-7.5%Bi-2%Ag-0.5%Cu alloys available as lead-free solders were used as reference examples. The flux was a mixture of rosin and methanol. The solder wettability test was conducted at a temperature of 230°C for a dip time of 5 s and with a dip depth of 2 to 3 mm.

(2) Solder spreadability

Solder spreadability was determined by heating a specimen to 230°C, placing a certain amount of the H63A solder (with the flux) on the specimen, and measuring the solder spread area on the specimen after a specified length of time.

2.7 Whisker evaluation

The formation of whiskers was evaluated by forming a specimen into a cup with a diameter of 5 cm and depth of 3.3 cm to produce working compressive stress in the inside surface for acceleration of whisker formation, and examining the surface by a scanning electron microscope at 3 to 6 months after humidity cabinet test with 60°C and 90%RH.

3. Experimental Results

3.1 Cross-sectional structure of coating

Fig. 2 shows the cross-sectional structures analyzed by the GDS of Zn-Sn-Ni alloy-coated steel sheet (Zn = 0.4 g/m^2, Sn = 4.0 g/m^2, Ni = 0.4 g/m^2) before and after the thermal diffusion treatment. The thermal diffusion conditions applied to the material are indicated by the heating-cooling curve of Fig. 1. As evident from Fig. 2, the Zn, Sn, and Ni layers are sequentially recognizable from the surface downward before the thermal diffusion treatment, although the interfaces between the layers are not clear. The structure is drastically changed after the thermal diffusion treatment. Especially, the outermost Zn layer diffused through the intermediate Sn layer to reach the lowest

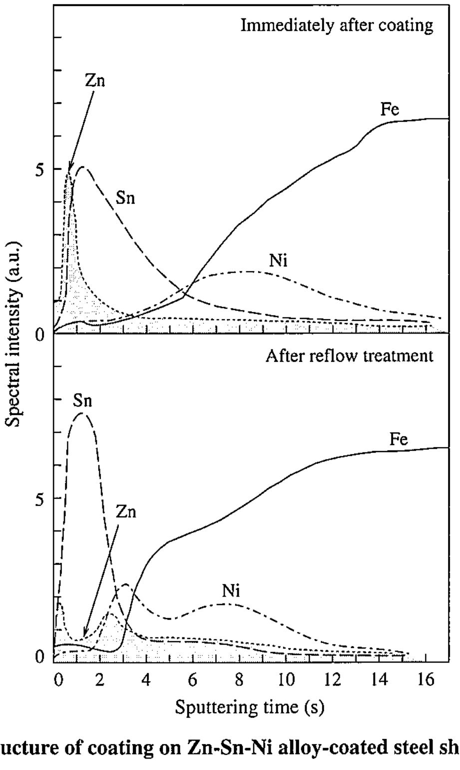


Fig. 2 Structure of coating on Zn-Sn-Ni alloy-coated steel sheet (GDS)

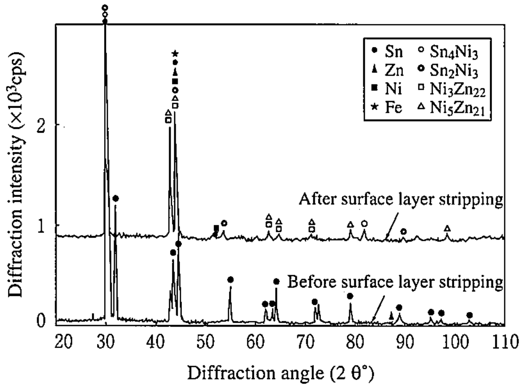


Fig. 3 **Structure of coating on Zn-Sn-Ni alloy-coated steel sheet (X-ray diffraction)**

Ni layer. Another characteristic is that the spectral intensity of Sn is extremely high after the thermal diffusion treatment.

A specimen was galvanostatically electrolyzed in a 1 N hydrochloric acid solution. The electrolytic stripping of the coating was interrupted at the point of inflection where the surface potential greatly changed. The X-ray diffraction results of the specimen before and after the electrolytic stripping of the upper layer are given in **Fig. 3**. The diffraction peaks of the Zn-Ni alloy are conspicuous near the interface between the steel base and the coating. Some diffraction peaks of the Sn-Ni alloy are also observed.

From the above results, it is estimated that the Zn-Sn-Ni three-layer thermal diffusion alloy coating consists of the upper layer of a Sn-Zn eutectic alloy and the lower layer of Zn-Ni and Sn-Ni intermetallic compounds.

Since the formation of the Sn-Fe alloy layer is generally governed by the inter-granular diffusion of Sn and Fe at the grain boundaries of the steel base, the diffusion rate is very fast. Consequently, it is estimated that the Sn-Fe alloy layer is formed as soon as the Sn layer is melted. With the Zn-Sn-Ni three-layer coating, the presence of the Ni layer between Sn and Fe is considered to retard the diffusion of Sn and Fe and to inhibit the formation of the Sn-Fe alloy.

In the thermal diffusion treatment temperature range of 250 to 350°C, Sn is melted, and the solution of Ni and Zn in the molten Sn layer is considered to take place. From the Sn-Ni and Sn-Zn binary alloy phase diagrams[4)], it is evident that in this temperature range, Ni melts little in the Sn liquid but Zn melts significantly in the Sn liquid. The Sn-Zn binary alloy phase diagram[4)] shows that 35 atomic percent Zn melts in the Sn liquid at 300°C. This value is equivalent to the proportion that all Zn melts in the Sn liquid in the case of the Zn-Sn-Ni three-layer coating in this report.

In the thermal diffusion treatment, a Sn-Zn solid solution forms first, and the reaction between the Sn-Zn molten layer and the underlying Ni layer then starts. As already described, the reaction between the Sn layer and the Fe base metal is inhibited by the Ni layer. As a result, the Zn-Ni alloy and the Sn-Ni alloy form at the interface between the Sn-Zn molten layer and the Ni layer. Most of the Sn-Zn molten layer solidifies as Sn-Zn eutectic on the cooling process. For this reason, Zn, which was the outermost layer when the coating was applied, is considered to diffuse through the intermediate Sn layer to the lowest Ni layer to form the Zn-Ni alloy.

3.2 Corrosion test results

Fig. 4 shows the formation of red rust by salt spray test on precoated steel sheets. The thermal diffusion Zn-Sn-Ni alloy-coated steel sheet has the formation of red rust controlled to nearly 0% as compared with the #50 tin plate. This result means that the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet is markedly improved in corrosion resistance.

In the electrochemical measurements, the natural electrode potential of the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet is equal to or slightly higher than that of the electrolytic tin plate. Although the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet was not expected to have a sacrificial protection capability like the electrolytic tin plate, it clearly exhibited such a capability in actual accelerated corrosion tests, and its corrosion resistance is much higher than that of the electrolytic tin plate. **Fig. 5** shows the cathodic polarization characteristics of the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet and the #50 electrolytic tin plate. As compared with the #50 electrolytic tin plate, the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet has larger polarization resistance and exhibits a lesser increase in current from –0.35 to the vicinity of –1.2 V vs. SCE. Generally, the current of –1.0 V vs. SCE on the electrolytic tin plate is said to be attributable to the reduction of oxygen on the steel surface. This current increase is not observed for the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet, probably because the thermal diffusion Zn-Sn-Ni alloy coating excels in uniform adherence and is relatively free from pinholes and other defects.

As discussed above, the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet is considered to exhibit much higher corrosion resistance than electrolytic tin plate of the same coating weight, firstly because Zn alloyed with Sn or Ni sacrificially protects the steel base against corrosion and secondly because the thermal diffusion Zn-Sn-Ni alloy coating excels in uniform coverage.

3.3 Solderability evaluation

Fig. 6 shows the Sn-Pb solder wettability and spreading test results of the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet, #50 tin plate, and terne sheet. The thermal diffusion Zn-Sn-Ni alloy-coated

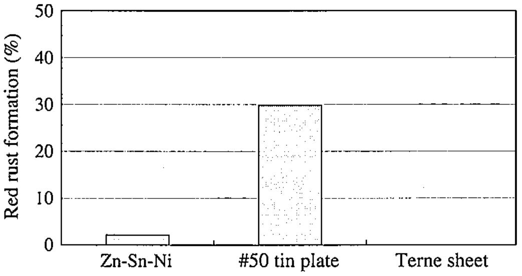


Fig. 4 **Corrosion resistance comparison of precoated steel sheets (72 h of salt spray test)**

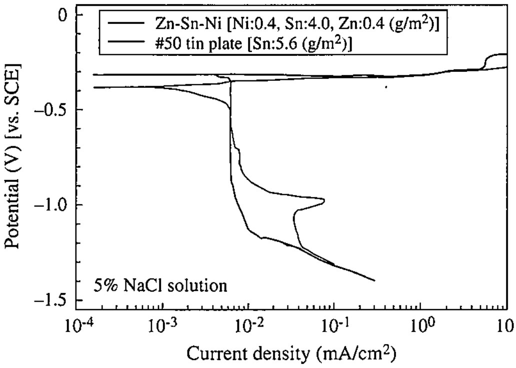


Fig. 5 Polarization characteristics of Zn-Sn-Ni alloy coating

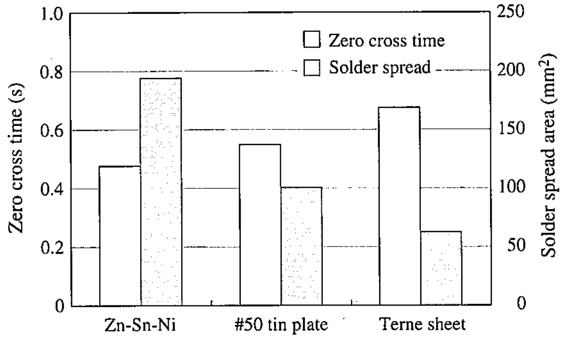


Fig. 6 Solderability comparison of precoated steel sheets (Pb-Sb solder)

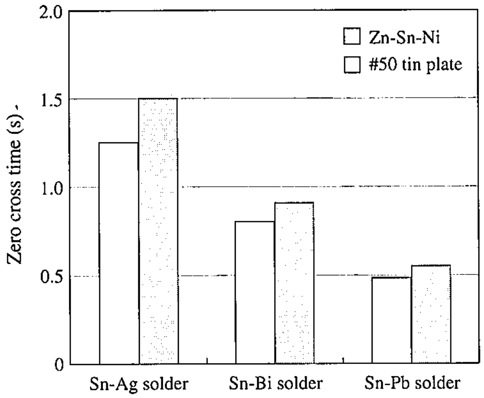


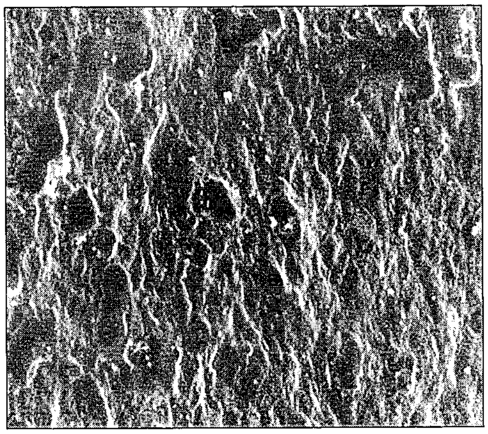
Fig. 7 Wettability comparison of precoated steel sheets with led-free solders and conventional solder

steel sheet has solderability equal or superior to that of the #50 tin plate and terne sheet. One characteristic of the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet is its excellent solder spreadability. This is probably because the melting point of the thermal diffusion Zn-Sn-Ni alloy coating with a Zn/Sn ratio of 10.0 wt% is 198°C as is obvious from the Sn-Zn binary alloy phase diagram and is lower than 232°C for Sn and about 300°C for the terne sheet.

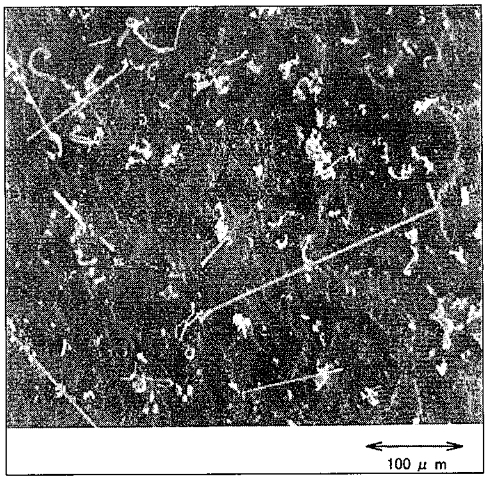
The solder wettability of the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet was tested using Sn-Ag and Sn-Bi alloys, studied as typical alloy compositions for lead-free solders. The results are given in **Fig. 7**. The zero cross time changes with the melting point of the alloy used (about 220°C for the Sn-Ag alloy and about 200°C for the Sn-Bi alloy) and tends to become longer than with the conventional Sn-Pb solder (melting point of 186°C). The thermal diffusion Zn-Sn-Ni alloy-coated steel sheet exhibits better wettability in each solder bath than the #50 tin plate and is considered to be acceptable as far as solder wettability is concerned.

3.4 Whisker resistance evaluation

One of the important properties required of the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet as material for electronic parts is whisker resistance. Particularly in recent years, electronic parts have decreased in size and increased in the probability of circuit shorts when tin whiskers are formed. The whisker resistance of tin-coated steel sheet and tin alloy-coated steel sheet has been studied in detail[5-7]. Various improvements, including increasing the coating thickness, relieving the stress in the coating by heat treatment, and alloying, are proposed. The mechanism of whisker growth is also investigated by many researchers.



(a) Zn-Sn-Ni alloy-coated steel sheet



(b) #50 tin plate

Photo 1 Comparison of whisker formation

Photo 1 shows the whisker formation of the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet as compared with the #50 tin plate. The thermal diffusion Zn-Sn-Ni alloy-coated steel sheet had no whiskers that were observed in the #50 tin plate. This is probably because the alloying of tin with zinc inhibits the diffusion of tin required for the formation and growth of whiskers as generally said[7].

4. Conclusions

The coating structure of the Zn-Sn-Ni alloy-coated steel sheet produced by the thermal diffusion process and its properties have been investigated. The following findings were obtained:

1) The thermal diffusion alloy coating obtained by sequentially depositing nickel, tin, and zinc on steel strip and heating the steel strip to the temperature at which the tin melts consists of the lower layer of Zn-Ni and Sn-Ni alloys and the upper layer mainly composed of a Sn-Zn solid solution.
2) The thermal diffusion Zn-Sn-Ni alloy-coated steel sheet has higher corrosion resistance than an electrolytic tin plate of the same coating weight. This is probably firstly due to the sacrificial protection afforded by zinc, some of which dissolves in tin and some of which alloys with nickel, and secondly due to the nickel pre-plating that improves the uniform coverage of tin.
3) Concerning solderability, the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet has better solder wettability and spreadability

than conventional terne sheet and electrolytic tin plate. This is probably because the surface layer of the Zn-Sn-Ni alloy coating is a Sn-Zn eutectic alloy of low melting point.

4) Concerning whisker resistance, the thermal diffusion Zn-Sn-Ni alloy-coated steel sheet had no whiskers at all as compared with the electrolytic tin plate and was equivalent to the terne sheet. This is probably because the alloying of tin with zinc inhibits the diffusion of tin.

The thermal diffusion Zn-Sn-Ni alloy-coated steel sheet was commercialized in 1991, is now used in semiconductor cases and electronic part shield cases and frames, and is expected to find increasing applications in response to mounting needs for freedom from lead.

Referance

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