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# SOC-free, Zn–Sn–Ni-alloy-coated Steel Sheets for Electronic Devices

Kiyokazu ISHIZUKA\* Koji KAWANISHI Takehiro TAKAHASHI

# Abstract

Zn-Sn-Ni alloy coated steel sheet produced by thermal diffusion of electroplated Ni, Sn, Zn triple layers has better corrosion resistance and lower growth rate of tin wiskers compared to tinplate. It also has excellent solderability, surface conductivity, and electromagnetic shielding performance. SOC (Substances of Concern) free Zn-Sn-Ni alloy coated steel sheet is suitable for use in electronic devices.

# 1. Introduction

Coated steel sheets for electronic devices are required in addition to high strength and corrosion resistance for use in device bodies in order to have good surface electric conductivity and solderability. Pb-Sn-coated sheets, known as terne-coated sheets, have been used for these applications since long. When steel sheets without metal coating are used for such parts, there are often cases where parts are coated with a Sn-Pb alloy (solder plating) after being pressed into final shapes.

In response to the latest requirement to eliminate the use of Pb, some users began to use electrolytically Sn-coated sheets (tinplates) in place of tern sheets or switched to apply Sn coating to the formed parts instead of Sn-Pb coating. Over time, however, acicular crystals (whiskers) of Sn grow from Sn coating layers to lengths of several hundred micrometers to some millimeters, causing problems of short circuiting to circuit terminals. In addition, since tinplates do not have sufficient corrosion resistance because they do not exhibit sacrificial corrosion protection in the environments of electronic devices, the use of tinplates has been limited to specific parts.

To solve the above problem by alloying Sn with other metal elements, Nippon Steel & Sumitomo Metal Corporation devised a method in which steel sheets are coated with layers of different metal elements and then the metals are thermally diffused to form alloy layers. As a result, the company has developed Zn-Sn-Ni-coated sheets by separately depositing layers of Ni, Sn, and Zn on steel sheet surfaces in this order and then heating the sheets to have the metal layers form alloys through diffusion; this product was found to solve the problems of tinplates and has been commercially launched in the market.<sup>1,2)</sup> Thereafter, a special phosphate treatment has been developed for the new alloy coating, and the developed product has become free of substances of concern (SOC). This paper reports the characteristics of the developed SOC-free steel sheets coated with the Zn-Sn-Ni alloy.

## 2. Tests

#### 2.1 Specimens

The developed product coated with the Zn-Sn-Ni alloy is manufactured by plating steel strips sequentially with Ni, Sn, and then Zn through an electrolytic tinning line (ETL), then having the coating metal elements form alloys through thermal diffusion in the heating and reflowing section of the ETL and finally applying SOC-free phosphate treatment. The coating weights of the three elements are changeable according to final application: Zn from 0.1 to 0.6 g/m<sup>2</sup>, Sn from 3 to 15 g/m<sup>2</sup>, and Ni from 0.1 to 0.7 g/m<sup>2</sup>. When high corrosion resistance is required, it is desirable to increase the coating weight of Zn. Unless specified, the specimens used for the test reported herein were coated with Zn, Sn, and Ni in coating weights of 0.1, 10, and 0.1 g/m<sup>2</sup>, respectively. (The specimens of the developed product are hereinafter called the Zn-Sn-Ni specimens.)

Tinplates of the same thickness (#25) and electrolytic galvanized sheets with chromate-free treatment were used as comparative materials (hereinafter called the Tinplates and the EG specimens, respectively). Most of the EG specimens had Zn layers 20 g/m<sup>2</sup> in coating weight with highly corrosion-resistant organic films on top of the Zn layers; for some test items, EG specimens coated with inorganic, highly electrically conductive films were used.

\* Senior Researcher, Hirohata R&D Lab.
1 Fuji-cho, Hirohata-ku, Himeji City, Hyogo Pref. 671-1188

#### 2.2 Test methods

2.2.1 Surface analysis

The sheet surfaces were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI5600 made by Ulvac-Phi Inc. MgK $\alpha$  was used as the X-ray source, and the diameter of the analysis area was set at 0.8 mm. The measurement was conducted on the outer surface and up to a depth of 30 nm (in terms of SiO<sub>2</sub>) after sputtering.

## 2.2.2 Corrosion resistance

Salt spray test (SST) with 5%NaCl solution was conducted at 35°C using specimen sheets masked at the cut edges and the back sides with polyester tapes, and the percentage area of rust was evaluated after a prescribed time of the SST.

# 2.2.3 Wettability with solder

Wettability balance test was conducted using a multisolderability tester SWET-2100 made by Tarutin-Kester Co. Ltd. to measure the time for wetting with solder (zero-cross time). The composition of the solder was 96.5%Sn-3.0%Ag-0.5%Cu. A rosin flux was used for the measurement, and the solder bath temperature was 245°C. The measurement was performed twice on each specimen: before and after holding it in an atmosphere at moisture saturation at 100°C for 8 h to have an oxide film form on the surface.

2.2.4 Surface electric conductivity (contact resistance)

A contact simulator CRS-1 of Yamasaki-Seiki Co., Ltd. was used to measure the contact resistance under a contact load of 1 N. 2.2.5 Shielding of electromagnetic waves

The electromagnetic wave shielding properties were measured by the I/O ratio method using the network analyzer mentioned in another atusy.<sup>3)</sup> A gasket was placed along the edge of an opening of a test device, and each specimen sheet,  $150 \times 150 \text{ mm}^2$  in size, was placed on the gasket to cover the opening completely. Leakage electromagnetic waves were measured with and without a 1220-g weight of Teflon on the specimen, and the electromagnetic attenuation with the specimen was determined in dB. The shielding effects of each specimen were evaluated by comparing the attenuation thus measured with that of the case of an ideal shielding, where the opening was closed with a copper sheet and the edges of the sheet were sealed completely with copper foil tapes. Here the attenuation in the ideal case was defined as 100, and the shielding effects were measured at 350 MHz.

2.2.6 Resistance to whisker development

The development of Sn whiskers was evaluated in the following manner:

In test condition (a), each specimen sheet was drawn into a cup 50 mm in diameter and 33 mm in depth, held in 90% relative humidity at 60°C for 1000 h, and the whisker development was observed through a scanning electron microscope (SEM) at the inner surface at the cup bottom that underwent compressive stress.

In test condition (b), the specimen sheets were subjected to 0-T bending (180° bending without gaps between faces), held in 85% relative humidity at 85°C for 1 000 h, and the whisker development was observed through the SEM at the top outer face of the bending.

# 3. Test Results

## 3.1 Surface analysis by XPS

The XPS results of the Zn-Sn-Ni specimens are given in **Fig. 1**. On the surface of the Zn-Sn-Ni coating, there were P oxides originating from the chemical treatment and Sn oxides from the coating alloy. At a depth of about 10 nm from the surface, there were no oxides, neither of P nor Sn, and Sn and Zn existed in the metallic state, which indicates that the oxide film was approximately as thin as 10 nm. Owing to the very thin oxide film, the good surface conductivity is maintained while discoloration and corrosion are effectively prevented.

#### 3.2 Corrosion resistance at SST

The rusted areas of the specimens after the SST for 8, 24, and 48 h are compared in **Fig. 2**. While the Zn-Sn-Ni specimens had no red or white rust and they did not discolor after 8 h of the SST, small spots of red rust appeared after 24 h. The corrosion protection effects of the Zn-Sn-Ni coating are presumably due to the sacrificial protection of Zn and prevention of pinholes due to the homogeneous cover by the primer coating of Ni.<sup>1, 2)</sup> Since tinplates do not have any sacrificial protection effects, spots of red rust were found on the Tinplates as early as after 8 h of SST. In contrast, the EG specimens did not have rust or discoloration after 48 h of SST. The above results indicate that, although inferior to the EG, the Zn-Sn-Ni is superior



Fig. 1 Results of XPS (P 2s spectra, Sn 3d spectra, Zn LMM spectra)



to the Tinplates in terms of corrosion resistance and is considered suitable for application to electronic devices in normal use conditions.

#### 3.3 Solder wettability

The zero-cross times of the specimens with the Sn-Ag-Cu solder are given in **Fig. 3**. The wettability of the Zn-Sn-Ni specimens was as good as or better than that of the Tinplates either before or after the 8-h holding. This is presumably due to the facts that the outermost oxide layer of the Zn-Sn-Ni specimen was as thin as shown in Fig. 1, and that the melting point of the outermost layer, in which Zn was in solid solution in Sn, was lower than that of pure Sn.<sup>1,2)</sup> Note that the EG specimens did not get wet with the solder in 10 s. This was largely because of the properties of the coating layer because the EG sheets used for the present tests had organic resin coating films for enhancing corrosion resistance. With coating films containing an additive compatible with the flux,<sup>4)</sup> the EG sheets would have exhibited good wettability with solder.

### 3.4 Surface electric conductivity

The results of the test simulating the resistance of electric contacts are shown in **Fig. 4**. The Zn-Sn-Ni specimens demonstrated contact resistance as low as that of the Tinplates. The contact resistance of the EG specimens was measured either with organic, corrosion-resistant treatment films, or inorganic, electro-conductive ones. The contact resistance of the Zn-Sn-Ni specimens was even lower (better in electric conductivity) than that of the EG with inorganic, electro-conductive films. This is presumably because of the thin surface oxide layer of the former, and the soft Sn top coating layer slightly deforming under the contact pressure to increase the contact area.

## 3.5 Shielding of electromagnetic waves

Figure 5 shows the evaluation results of the shielding effects of



\* High electroconductive, Inorganic

Fig. 5 Comparison of electromagnetic shielding effectiveness

electromagnetic waves with and without the weight on the specimen. With the weight, the shielding effects of the three types of specimens was 100% or equal to the case where the opening was covered completely with a copper sheet, evidencing the high shielding potential of coated steel sheets; note that the EG specimen used here was coated with inorganic, electro-conductive films. Without the weight, the shielding effects of any of the specimens lowered, but to different extents; the shielding effects of the Zn-Sn-Ni were better than those of the Tinplates or the EG with electroconductive films. The electromagnetic shielding performance of device bodies of coated steel sheets is considered to depend on the transmission impedance of sheet joints, and the impedance decreases as the thickness of the insulating coating film decreases, and the skin depth of the metal material increases.<sup>5,6)</sup> The excellent electromagnetic shielding effects of the Zn-Sn-Ni sheets are probably due to high conductivity owing to the very thin oxide film on the surface and Zn and Sn, which have large skin depths in the coating layer.

As explained above, for device bodies structured such that it is impossible to impose heavy loads on sheet joints, Zn-Sn-Ni-coated sheets are expected to be better than the other types of coated sheets in terms of the shielding performance of electromagnetic waves.

# 3.6 Resistance to whisker development

**Figure 6** compares the maximum lengths of the tin whiskers that grew on the specimens under test conditions (a) and (b). Whiskers exceeding 100  $\mu$ m in length were found to grow under condition (a) on the Tinplate specimen (**Photo 1** is an SEM photomicrograph of such an example). In contrast, the whiskers on the Zn-Sn-Ni specimens did not grow to exceed several micrometers. This high whisker resistance of Zn-Sn-Ni coated sheets is presumably due to the fact

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Fig. 6 Comparison of maximum whisker length



Photo 1 Example of tin whisker, Tinplate, Condition (a)

that, as is widely known, Sn forms an alloy with Zn, and thus Sn diffusion is insufficient for the formation and growth of whiskers.<sup>7</sup> Note that the comparative EG specimen had too much white rust (Zn oxide) under condition (a) to observe whiskers through the SEM.

Sometimes tin whiskers, tens of micrometers long, can be found on Zn-Sn-Ni coating sheets, depending on the conditions of working and atmospheric temperature and moisture (for instance, test condition (b) is considerably severe), if not as many and long ones as on tinplates. Nippon Steel & Sumitomo Metal reviewed the alloy composition of the Zn-Sn-Ni coating to better prevent the whisker growth under such adverse conditions; the column of Zn-Sn-Ni (advanced) in Fig. 6 represents the result of the review. In this improved coating, the alloy layer at the interface with the base metal has such a homogeneous structure that the stress accumulation inside the deformed parts while working is mitigated. As seen on the right-hand side of Fig. 6, the improved product exhibits a better whisker resistance than that of the original Zn-Sn-Ni specimen.

Although it is difficult for the Zn-Sn-Ni coating to be completely free of tin whisker development as explained above, especially under severe conditions; it is possible to significantly decrease the whisker development from the level of ordinary tinplates.

## 4. Closing

The steel sheets coated with the Zn-Sn-Ni alloy presented herein have been launched in the market under the trade name of ECOTRIO<sup>™</sup> and widely used for semiconductor casings, shield cases, frames for electronic devices, etc. The demand for thin sheets of high-strength materials is increasing in the field of electronic devices, and Nippon Steel & Sumitomo Metal is responding to the growing demand using the developed product.

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Kiyokazu ISHIZUKA Senior Researcher Hirohata R&D Lab. 1 Fuji-cho, Hirohata-ku, Himeji City, Hyogo Pref. 671-1188



Takehiro TAKAHASHI Senior Researcher Hirohata R&D Lab.



Koji KAWANISHI General Manager, Head of Dept. Electrolytic Tinning Sheet Quality Control Dept. Production & Technical Control Div. Hirohata Works