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Development of Cross-Sectional TEM Analysis Techniques for Coated Steel Sheets

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Abstract:

A new ultramicrotomic analytical transmission electron microscopy (ATEM) was developed analyze the cross-sectional morphology, composition, and crystal structure of coated steel sheets at a resolution of the order of a nanometer. The new analytical technique cuts a ultrathin section of about 20 nm thickness from a coated steel sheet sample with a ultramicrotome having a diamond knife, and observes the ultrathin specimen under a transmission electron microscope. Ultramicrotomy has been traditionally used to prepare ultrathin-foil specimens from soft materials like biomaterials and resins. Application of this technique to an extremely hard coated steel sheet called for the cutting method to be improved and the size of the cut face to be reduced to about one-hundredth from the conventional size. When ultrathin sections of two-layer zinc-iron alloy-electroplated steel sheet were examined by the new technique, it was confirmed that despite the wrinkly deformation of the base steel surface, the zinc-iron alloy electroplated coating is in a condition allowing microstructural analysis. When the cross-sectional microstructure of Zn-Ni-SiO_2 composite-coated steel sheet was analyzed, it was found that SiO_2 particles change into one of the four codeposition conditions, namely, lamellar coagulation, granular coagulation, uniform dispersion and surface segregation, depending on the coating conditions.

1. Introduction

Zinc- and zinc alloy-coated steel sheets are widely used in automobile bodies. As their consumption in the auto-body panel application has increased under increasing severity of performance requirements in recent years, steelmakers have modified and added production lines, and developed new products to meet the needs of automakers. Among the zinc- and zinc-alloy coated sheet products commercially produced now are thin organic composite-coated zinc-nickel alloy-electroplated steel, two-layer zinc-iron alloy-electroplated steel, hot-dip galvannealed steel, and two-layer hot-dip galvannealed steel. Composite-coated steel with codepo-

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sition of metal oxide[1-3], zinc-chromium alloy-coated steel[4], and zinc-manganese alloy-coated steel[5] are studied as next-generation corrosion-resistant steel sheets. In terms of cross-sectional structure, these zinc alloy-coated steels consist of 2 to 10 μm thick zinc alloy coating, 0.1 μm thick chromate film, and 1 μm thick organic film. These layers have finer cross-sectional structures themselves. For example: a zinc alloy layer near the interface of a hot-dip galvannealed coating; codeposition of metal oxide particles of about 0.02 μm size in a composite electroplated coating; and the dispersion of SiO_2 particles of about 0.02 μm size in a chromate film. In this way, coating modification is proceeding in the directions of alloying and multiple laying. Controlling the cross-sectional micro structure of zinc- and zinc-alloy coated steels is important in improving the corrosion resistance and other properties of their coatings.

Establishment of structure control techniques is prerequisite to the possession of structure analysis techniques. Historically, various techniques have been used, including optical microscopy, electron probe microanalysis (EPMA), glow discharge spectroscopy (GDS), X-ray diffraction (XRD), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). These techniques, however, fail to acquire cross-sectional information on the morphology, composition, and crystal structure of the above-mentioned multilayer coatings with a high resolution, prompting the call for the development of new analytical techniques with resolutions of the order of a nanometer.

The authors noted the capability of transmission electron microscopy (TEM) to measure the morphology, composition, and crystal structure of the specimen by TEM, energy-dispersive spectroscopy (EDS), and electron diffraction, respectively, all at one site of the specimen with a high resolution. They attempted to apply this capability of TEM to the cross-sectional structural analysis of coated sheet steels. First, ultramicrotomy was studied as the method of preparing cross-sectional thin-foil specimens, a key point in the analytical technique of interest. The structure of Zn-Ni-SiO_2 composite-coated steel sheet was analyzed by the new technique.

2. Cross-Sectional TEM Technique

2.1 Position of TEM among structural analysis techniques

Fig. 1 compares various structural analysis techniques in the area of coverage and depth of information obtained. X-ray diffraction (XRD) and scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS), which are widely used in the structural analysis of coated steel sheet, have a resolution of the order of a micrometer. Scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES) provide a sufficient resolution in either analysis coverage or depth, but are limited to one or two types of information, such as morphology or composition, and are unsatisfactory as analytical techniques for coated steel sheets. In recent years, field-emission transmission electron microscopy (FE-TEM) has been developed as a new technique to obtain information about morphology, compostion, and crystal structure at one site of the specimen with high resolutions of several Angstroms, several nanometers, and several nanometers, respectively. TEM is thus known to be an appropriate technique for analyzing the submicron structure of coated steel sheet.

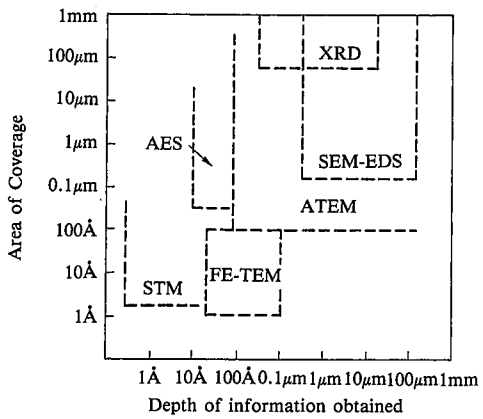

Fig. 1 Positioning of techniques for structural analysis

2.2 Study of method for preparing thin-foil specimens

In the TEM method, specimen preparation is extremely important, and the success of thin-foil specimen preparation is a key point. The specimen for TEM observation must be prepared as a thin foil of about 0.1 μm or less thickness so that the electon beam can transmit it. Generally, electropolishing, chemical polishing, ion beam polishing, and microtomy are known as methods for preparing thin-foil specimens from metallic materials. Except microtomy, these methods are widely used for thinning specimens of metallic materials, including ferrous materials. Microtomy is limited to the preparation of thin-foil specimens from soft materials like biomaterials, although it is used for preparing thin-foil specimens from some aluminum alloys and nickel coatings[6,7]. For various reasons, these techniques are inconvenient for preparing cross-sectional thin-foil specimens from zinc- and zinc alloy-coated steel sheets and have not produced any good cross-sectional thin-foil specimens in the past. Zinc and iron are widely different in oxidation-reduction potential, so that zinc alone is preferentially dissolved during electropolishing or chemical polishing. This selective polishing makes it impossible to prepare a cross-sectional thin-foil specimen in which the coating coexists with the base steel. If the coating is a zinc alloy, the zinc alone dissolves to run the risk of changing the coating structure itself. With ion beam polishing, zinc and iron are so different in sputtering efficiency that selective polishing sometimes occur, with the specimen being recrystallized or damaged by ion bombardment[8,9]. Microtomy cuts a specimen from a bulk material with a sharp diamond knife and is free from the problems noted above, but is likely to involve the deformation of the specimen structure during cutting (compression, chatter, wrinkle, and knife marks) and to encounter difficulty in cutting hard metallic materials.

Since microtomy is least liable to change the quality of materials, except for mechanical deformation due to specimen preparation, among the existing techniques, the authors judged microtomy to be most advantageous as a technique to cut ultrathin sections from bulk samples, although not field proven in thinning cut sections from coated steel sheet samples, and worked to establish the ultramicrotomic technique.

2.3 Preparation of ultrathin sections by microtomy

Microtomy cuts a ultrathin section from a bulk sample by feeding a vertically rocking arm with the sample toward a diamond knife in increments of 1 to 100 nm. The development of accurate microfeed mechanisms goes back to the reports of the thermal expansion feed method[10] and mechanical feed method[11] in

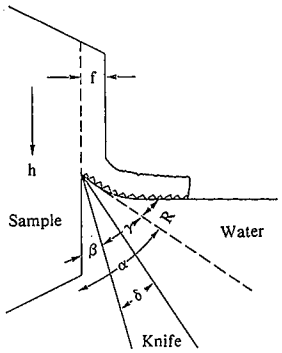

Fig. 2 Operating factors during cutting

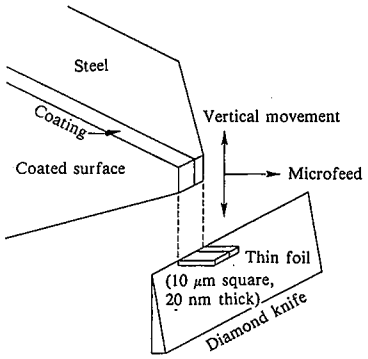

Fig. 4 Shape of sample face to be cut

1953. Today, an arm expanded by heating is used for the former method, while a lead screw or stepping motor is used for the latter. Several improved designs are marketed by several manufacturers.

2.3.1 Operating factors during cutting

When cutting a ultrathin section from a coated steel sample, it is important that the cross section containing the hard base steel and the soft coating be cut in minimum thickness and with minimum strain. Operating factors during cutting were identified, and optimum operating conditions were examined. These operating factors are schematically illustrated in **Fig. 2**. They are: i) sample feed f (cut thickness); ii) cutting speed h; iii) cutting angle α; iv) relief angle β; v) actual knife angle γ; vi) knife angle δ; and vii) knife boat-knife edge angle R. To obtain a good cut, the microtome must be operated under such conditions as to reduce the cutting resistance and friction. The cutting resistance was reduced by using a small sample and a knife of small edge angle. The cutting friction was reduced by filling the knife boat with water and making the water surface concave. Since R, α, β, γ, and δ depend on the water level of the knife boat and the diamond knife to be used, f and h and the sample shape as described later were adjusted as required. As the sample feed f was reduced, the strain of the obtained section was reduced, and the compression, chatter, and wrinkle marks were reduced. The sample feed f should preferably be set at about 20 nm considering the sharpness of the knife edge. Decreasing the cutting speed h proved effective in reducing the impact on the knife edge to prevent damages to it.

2.3.2 Sample shape and cuttability

The shape of the sample is as important as the performance of the knife. It is no exaggeration to say that whether or not the sample can be properly cut depends on whether or not the sample is properly shaped. Samples cut from biological materials, for example, are embedded in a resin and trimmed to a face of about 0.5 to 1 mm square. For details, refer to the report of Sakai[6]. This conventional method cannot be used to cut a thin section from a coated steel sample because it is extremely hard. The new method described below was established[12]. An attempt was made to make the sample as small as possible to minimize the cutting resistance noted above. The sample was not embedded in a resin but was trimmed as shown in **Fig. 3**. A 5 mm by 15 mm sample is cut from a coated steel product, and one narrow face is ground into a sharp-angle point with a pair of nippers and a file. The sample is then fixed to a microtome and finish trimmed with a glass knife. **Fig. 4** shows the final shape of the sample face to be cut. The face to be cut is a rectangle or square, one side measuring about 5 to 10 μm long. The length of one side is about one-hundredth of that of conventional biological samples. When cutting a ultrathin section from the sample, the angle between the diamond knife and the sample is set as shown in **Fig. 4**. In other words, the sample face to be cut is set perpendicular to the edge of the diamond knife, so that the coating is not peeled when a ultrathin section is cut from the sample face. Usually, the sample is rotated about 10° to start the cutting operation from the base steel side and to facilitate the entry of the edge of the diamond knife into the sample.

2.3.3 Preparation and TEM observation of ultrathin sections

The ultrathin section cut from the sample floats on the surface of water in the knife boat. It is scooped onto a collodion-coated TEM grid, dried, and observed by TEM. The scooping is manually performed under a 70X stereoscopic microscope and involves the task of pulling the ultrathin section onto the TEM grid with the tip of an eyelash. Since the ultrathin section is extremely small with one side measuring only about 5 μm, it is often lost. Failures most frequently occur in this step of the entire procedure.

Specimens were observed under a JEOL JEM4000FX transmission electron microscope at an acceleration voltage of 400 kV. **Photo 1** shows a low-magnification TEM image of two-layer Fe-Zn alloy-electroplated steel sheet. Of 10 to 20 ultrathin sections obtained by continuous cutting and placed on the TEM grid, those with the best cut condition were examined. In **Photo 1**, two sec-

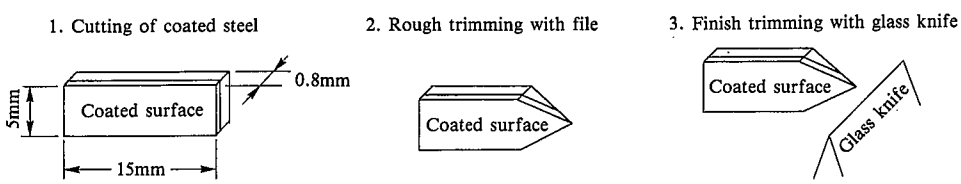

Fig. 3 Trimming method

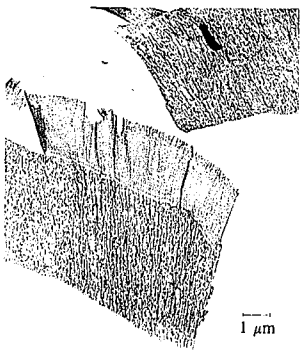

Photo 1 TEM image of two-layer Fe-Zn alloy electroplated steel sheet

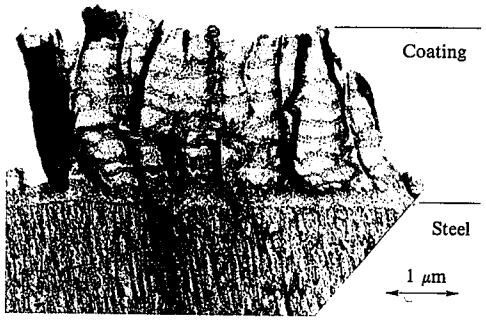

Photo 2 Cross-sectional TEM micrograph of Zn-12.1 wt% Ni-20.5 vol% SiO_2 composite-coated steel sheet

tions are shown adjacent to each other. The section at the center of the field of view is about 6 by 10 μm in size. The lower half of the section is the base steel, and the upper half is the coating. The coating is damaged on the left side, but is intact in the rest. The cutting direction is from the left to the right of the section (tilted 10° toward the base steel side). Chatter and wrinkle patterns are observed in the direction perpendicular to the cutting direction. These patterns are marked in the base steel, but are slight in the coating. This is probably because the base steel is a mild, deep-drawing grade, while the coating is a hard iron-zinc alloy. The coating reveals a lamellar structure produced during continuous electrolytic deposition and an upper iron-zinc alloy layer of about 0.3 μm thickness. The above results indicate that the ultrathin sections obtained by the new method are fully serviceable as TEM specimens.

3. Observation of Cross-Sectional Microstructure of Zn-Ni-SiO_2 Composite-Coated Steel Sheet[1,12,13]

Composite-coated steel sheet with oxide particles like those of SiO_2 dispersed in a zinc alloy coating is studied as coated steel product with excellent corrosion resistance. The oxide particles are extremely small at about 20 nm, so that their dispersion in the coating is difficult to determine. Analysis of the dispersed state of oxide particles is important in controlling the properties of the composite coating and clarifying the codeposition mechanism of the oxide particles. The relationship between the coating conditions and the dispersion of oxide particles was clarified through the observation of cross-sectional microstructure by TEM, and the particle codeposition mechanism was studied according to the results of observation. The findings obtained are described below.

3.1 Experimental procedure

Specimens were electrodeposited from an acid bath composed of zinc sulfate, nickel sulfate, and SiO_2 colloid (average particle size of 20 nm). The amount of codeposited SiO_2 in the coating was adjusted by changing the SiO_2 concentration of the bath, current density, and pH[12]. The composition of the deposited coating was determined by chemical analysis, and the cross-sectional structure of the coating, including the SiO_2 codeposited condition, was analyzed by the TEM technique.

3.2 Experimental results

Photo 2 shows a cross-sectional TEM image of the Zn-12.1wt% Ni-20.5 vol% SiO_2 composite coating. The cutting direction is from left to right, and chatter and wrinkle marks are observed in the direction perpendicular to the cutting direction. The cross section of the coating reveals a lamellar structure where bright and dark layers are periodically stacked. The layers measure 100 to 200 nm in thickness and vary in length in the horizontal direction. High-magnification TEM images of the lamellar structure are shown in **Photo 3**. The bright-field image shows that the bright layer is composed of coagulated particles of about 20 nm size. The particles are similar in average primary size to the SiO_2 particles added in the coating bath and are identified as those of SiO_2 according to the intense silicon peak in the EDS spectrum. Nickel and zinc peaks are seen in the EDS spectrum, an electron diffraction ring for the zinc-nickel alloy is obtained, and bright spots indicating the presence of alloy crystallites are observed in the dark-field image. These results mean that the bright layer is not composed of coagulated SiO_2 particles alone but is a mixture of SiO_2 particles and zinc-nickel alloy crystallites where the zinc-nickel alloy serves as binder for SiO_2. The dark layer was identified as the zinc-nickel alloy layer because little or no SiO_2 is detected and because the silicon peak height in the EDS spectrum is smaller than observed for the bright layer. Comparison of the EDS peak intensity ratio of zinc to nickel between the bright layer and the dark layer shows that the two layers markedly differ in the composition of the zinc-nickel alloy. The nickel content of the coagulated SiO_2 layer is about 6 times that of the alloy layer in terms of the peak intensity ratio.

From the above observations, it was found that SiO_2 is codeposited in the coating as coagulated to some extent, that the SiO_2 codeposition is produced with time fluctuations, resulting in the formation of a lamellar structure, and that the coagulated SiO_2 layers and the zinc-nickel alloy layers are widely different in the composition of the zinc-nickel alloy with SiO_2 affecting the zinc-nickel alloy electrodeposition reaction.

When coatings with different amounts of SiO_2 codeposition were similarly examined by TEM, four main types of coating structures were obtained as shown in **Fig. 5**. It was found that these coating structures depend on the amount of SiO_2 codeposition and that different coating structures can be produced by changing the coating conditions (such as pH, current density and bath SiO_2 concentration). As the amount of SiO_2 codeposition increases, the condition in which SiO_2 is codeposited changes from surface segregation to uniform dispersion, to granular coagulation, and to lamellar coagulation. This change depends on the magnitude of the coagulation reaction of SiO_2 at the cathode. The coagulation reaction is presumed to arise from the rise of pH at the interface between the cathode and the coating solution and from the dehydration reaction at the SiO_2 surface.

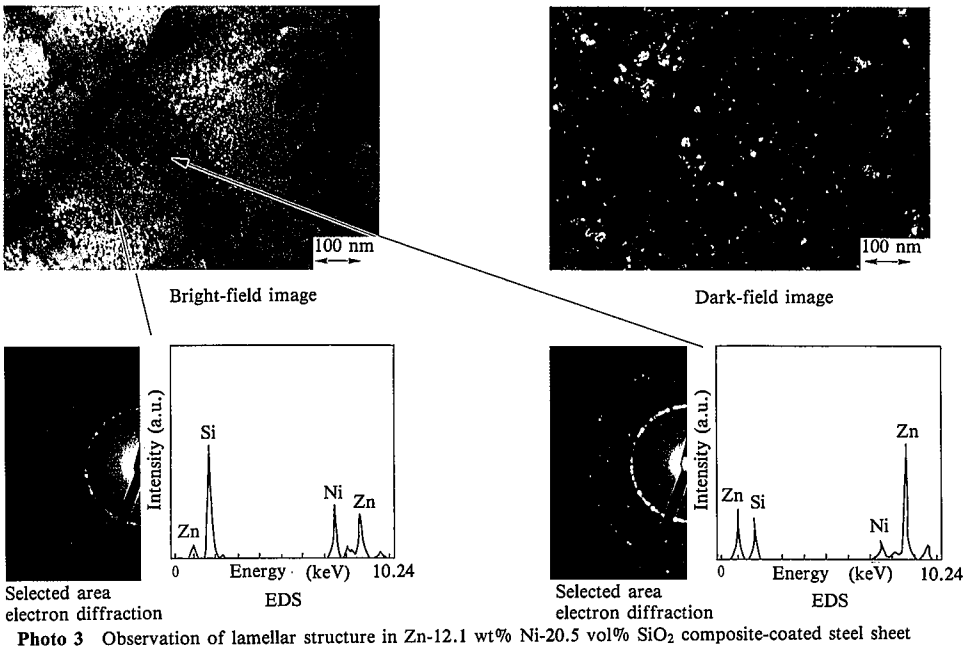

Photo 3 Observation of lamellar structure in Zn-12.1 wt% Ni-20.5 vol% SiO_2 composite-coated steel sheet

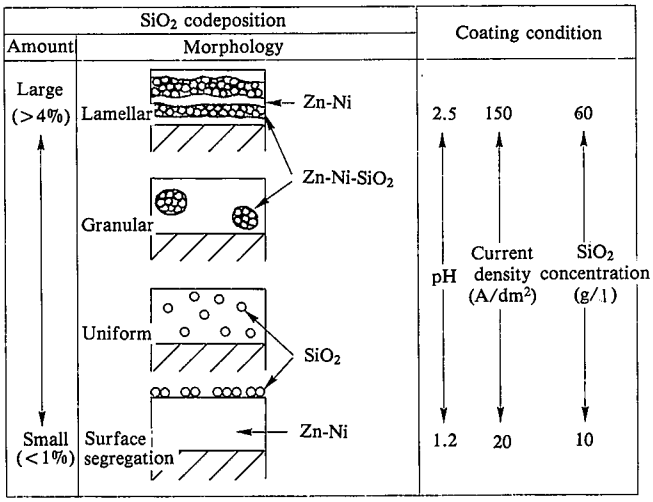

Fig. 5 Classification of coating structure

Increasing the pH, current density or SiO_2 concentration increases the ease with which SiO_2 coagulates at the cathode or in the coating bath.

4. Conclusions

The procedure for preparing cross-sectional thin-foil specimens of coated steel sheet by microtomy and examples of analysis of the cross-sectional fine structure of Zn-Ni-SiO_2 composite-coated steel sheet have been described above. The newly developed microtomic technique can be applied to preparing cross-sectional thin-foil specimens from coated steel sheet and other metallic materials, including commercial ones. It is expected to find widespread usage in the quality improvement of conventional coated steel sheet through detailed structural analysis, in the development of new coated sheet products, and in the structural analysis of other metallic materials. Field-emission transmission electron microscopy (FE-TEM), or TEM with a field-emission electron gun, has begun to be used on a full-fledged basis. The FE-TEM technique can observe lattice images with an EDS resolution more than 10 times higher than that of the conventional TEM method and is a powerful tool for analyzing materials having fine structures. The thickness of cross sections cut with the microtome is about 20 nm and too large for lattice images to be observed by FE-TEM. How to obtain thinner sections is a future issue. It is also necessary to check specimens for deformation or alteration on a lattice image scale.

Several published reports say that selective polishing during ion beam thinning can be prevented by devising a preliminary polishing (mechanical polishing) method or adjusting the ion irradiation method. To obtain desired results, it will be necessary to select techniques for thinning specimens to suit mechanical properties or cross-sectional structures of specific materials, so that thin-foil specimens can be prepared, examined and analyzed in better conditions.

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