Development of On-line Analysis Methods for Zinc Alloy Coatings for Automotive Use

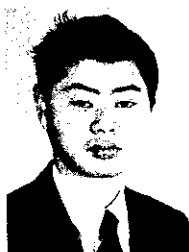Chiaki Kato, Yasuharu Matsumura, Akira Yamamoto, Toshio Irie

Synopsis：

On-line analysis methods, which analyze Zn alloy and organic resin coated steels for automotive panels, have been developed and employed in Kawasaki's galvanizing and coating lines. X-ray fluorescence spectrometry is applied to the analysis of Zn-Ni alloy electroplated coatings and electrolytes. For the analyses of Fe-P/Zn-Fe alloy electroplated double-layer coatings and hot-dip galvannealed coatings, X-ray diffraction is used in combination with X-ray fluorescence spectrometry to distinguish Fe in coating from that in the base steel. On-line thickness measurement methods for the thin organic resin top layers on Zn-Ni alloy coatings are also discussed.

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1 Introduction

Demand for precoated steels has increased with the need for enhanced corrosion protection of automotive bodies, which also require press formability, spot weldability, phosphatability, and paintability. Zinc alloy coatings which contain 10 to 20 wt.% of Ni or Fe, double-layer coatings consisting of an Fe rich alloy upper layer on the zinc alloy coating, and thin organic resin coated Zn-Ni alloy steels have been developed in order to improve these qualities of pure zinc or thick zinc rich organic coatings. Since the characteristics of these coatings depend strongly on alloy compositions and, especially in double-layer coatings, on the thicknesses of the top coating, changes in these variables must be controlled within a narrow range. For alloy electroplating, however, the deposited alloy composition changes with

operational variables such as electrolyte composition, which in turn changes with ion consumption in electroplating. In hot dip galvannealed steel, coating properties are more closely related to the degree of alloying than in Zn-Fe electroplating. The diffusion of Fe into Zn determines the Fe content of the coating and changes with the composition of the base steel, Al content of the Zn bath, and alloying temperature and time. Precise control of these operational variables to obtain the proper alloy composition is quite difficult in both the electroplating and galvannealing processes. Therefore, measurement of the chemical compositions of coatings in the width and length directions of the coated steel strip is an essential technique. Furthermore, measurement of the electrolyte composition is also needed.

A list of on-line analysis apparatuses installed in the coating lines of Kawasaki Steel Corp. and its subsidiary Kawatetsu Galvanizing Co. Ltd. is shown in Tables 1 and 2. The number of analysis items and methods has increased with the years, which is attributed to the development of new coatings, upgrades of coating qualities as well as advances in analysis techniques. When such devices were first installed, the coating was a single layer, consisting of a single element. In recent years, however, double layer coatings alloyed with Fe, which is analytically difficult to distinguish from the Fe of the base steel, have become important. Analysis methods mainly utilize X-ray techniques because of their excellent stability and easy maintenance, although these tech-

Table 1 On-line analysis apparatus for measuring coating weight and alloy content

Products	Coating line		Installation	Analysis items	Analytical method
Zinc and zinc alloy electroplating (Pure Zn / Zn-Ni / Zn-Fe / Double layers)	Hanshin	EGL	'84.7	Zn, Zn-Ni, Ni%	XRF (Wavelength-dispersive type)
	Mizushima #1 EGL		'87.4	Zn, Zn-Ni, Fe-P, Cr, Ni%	
	Mizushima #2 EGL*²		'91.	Zn, Zn-Ni, Cr, Ni%	
	Chiba	EGL	'87.12	Zn, Zn-Ni, Zn-Fe, Fe-P, Cr, Ni%, Fe%	XRD and XRF (with two take-off angles)
Galvanized and galvannealed coating	Tamashima	CGL*¹	'84.8	Zn, Zn+Fe, Fe%	XRD and XRF
	Chiba	#3 CGL*¹	'87.4	Zn, Zn+Fe, Fe%	
	Mizushima	CGL	'89.3	Zn, Zn+Fe, Fe%	
	Chiba	#2 CGL*²	'91.	Zn, Zn+Fe, Fe%	
Thin organic composite coating	Chiba	EGL	'88.8	Resin	IR (Filter type)
	Mizushima	MCL*²	'91.	Resin, Cr	IR (Filter type) and XRF

Notes XRF: X-ray fluorescence spectrometry   IR: Infrared absorption spectroscopy
XRD: X-ray diffractometry
*¹Kawatetsu Galvanizing Co., Ltd.   *²Operation is scheduled in 1991.

Table 2 On-line analysis apparatus for measuring concentration of electrolytes and various reagents in the solutions for electroplating and chemical treatment

Products	Coating line		Installation	Analysis items	Analytical method
Zinc and zinc alloy electroplating	Hanshin	EGL	'83.1	Zn, Ni, S, Ni, etc.	XRF (Microdroplet method with formed filter medium)
	Chiba	EGL	'85.4	Zn, Ni, Fe, Cr, P, etc.	
	Mizushima #1 EGL		'87.4	Zn, Ni, Fe, Cr, P, S, etc.	
	Mizushima #2 EGL*¹		'91.	Zn, Ni, Cr, P, S, etc.	

Notes XRF: X-ray fluorescence spectrometry
*¹Operation is scheduled in 1991.

niques have been adapted from their original simple uses to more complicated applications, including the combined measurement of the chemical and structural characteristics of coatings.

Recently, various on-line analysis methods, theoretically proposed and/or practically applied, for zinc alloy coatings were reviewed.[1] In this report, practical methods mainly developed by Kawasaki Steel are introduced and discussed. The contents include methods for Zn-Ni alloy electroplated coatings, hot-dip galvannealed coatings, electroplated Fe-P/Zn-Fe double-layer coatings, and organic composite coatings and electrolyte solutions.

2 Analysis Method for Zn-Ni Alloy Electroplating and Organic Coatings

2.1 Measurements of Coating Weight and Ni Content of Zn-Ni Alloy

In comparison with pure Zn coated steel, Zn-Ni alloy

electroplated steel sheets are known to show better corrosion resistance, spot weldability, and press formability. When the Ni content of the Zn-Ni alloy is between 10 and 14%, it consists of a single γ phase and shows the above mentioned excellent qualities.

For coating weight and Ni content analyses, two methods using an X-ray fluorescent technique have been developed. Fujino et al.[2] developed a balanced filter method which utilizes the difference in X-ray absorbability by two different filters. Kitayama et al.[3] developed a wavelength dispersive method which was introduced in Kawasaki Steel's electrogalvanizing lines. This method has the advantage of high resolution in wavelength, which is required for the analysis of alloy coatings.

In this method Zn and Ni X-ray fluorescence radiated from the Zn-Ni alloy and Fe X-ray fluorescence from the base steel are dispersed with analyzing crystals, as shown in Fig. 1. The intensities of these X-rays are measured, and the coating weights of Zn and Ni are determined respectively from the intensity ratio of Zn
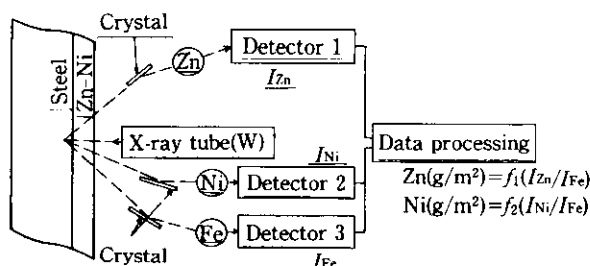
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Fig. 1 Wavelength dispersion method for Zn-Ni alloy
coating weight and Ni content analysis

Fig. 2 Resin thickness measurement by infrared
absorption method

to Fe and of Ni to Fe using calibration curves.

The accuracy of this on-line analysis method is about 0.2% for Ni content and 0.2 g/m² for coating weight. (In this report, accuracy is expressed by $\sigma_d = \sqrt{\Sigma d^2/(n-1)}$, where d equals the difference between the measured value with this technique and the value obtained by a wet chemical analysis, and n equals the number of samples.)

2.2 Resin Thickness Measurement of Organic Composite Coating

To guarantee a perforation corrosion resistance of ten years, a product in which a thin organic-silicate composite coating is applied over a chromated Zn-Ni alloy electroplated surface has recently been developed and is now in commercial application[4]. The thickness of this composite coating layer is on the order of 1 μm, and plays a critical role in determining the total characteristics of the product.

Honda et al.[5] proposed a β-ray backscattering method, in which β-rays are irradiated on the coating and the coating thickness is determined from the intensity of the backscattered β-rays, which varies with coating thickness. The analytical accuracy is 0.065 μm.

For thinner coatings, however, an infrared absorption method shows better accuracy and was introduced in Kawasaki's coating lines[6]. A schematic diagram of this method is shown in Fig. 2. Three optical filters, through which infrared rays of different wavelength penetrate, are set on a high speed rotating disc. Wavelength 2800~ 3000 cm⁻¹ is used to measure the absorption by stretching vibration of C-H in the methyl and methylene groups, while the other two wavelengths provide background. Infrared rays are irradiated on the coating to be measured through a polarizer which suppresses the interference between the light reflected from the bottom of the coating and that from the surface[7]. The coating thickness is determined from the absorbance of infrared rays of a specific wavelength, which are absorbed quantitatively by the coating. The accuracy of this analysis method is 0.023 μm at a line speed of 120 m/min, and measurement requires 0.64 s. Photo 1 shows the infrared absorption resin thickness analyzer installed in Chiba EGL.
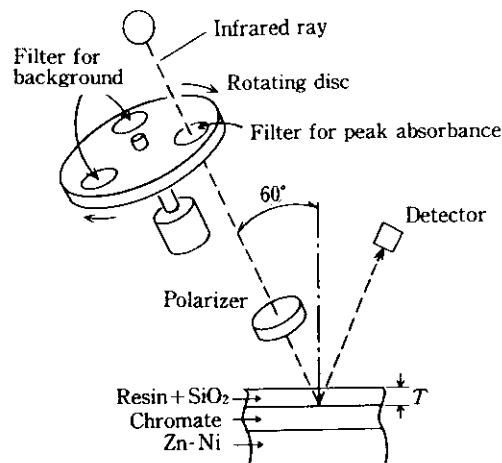
(a)
Side view
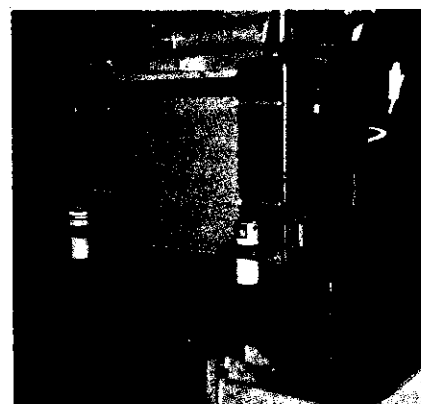
(b)
Close-up
view of the
measuring
head

Photo 1 Infrared absorption resin thickness analyzer

2.3 Ionic Concentration of Electrolyte Solution

Two methods have been developed to analyze electrolyte solutions. In one, X-rays are irradiated directly to the solution through a mylar film. Fluorescent X-rays radiating from the solution are then analyzed using a
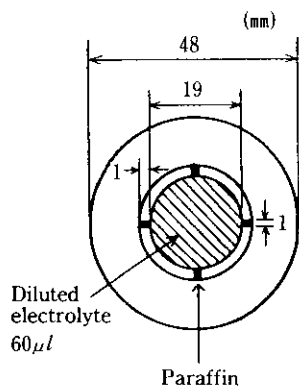
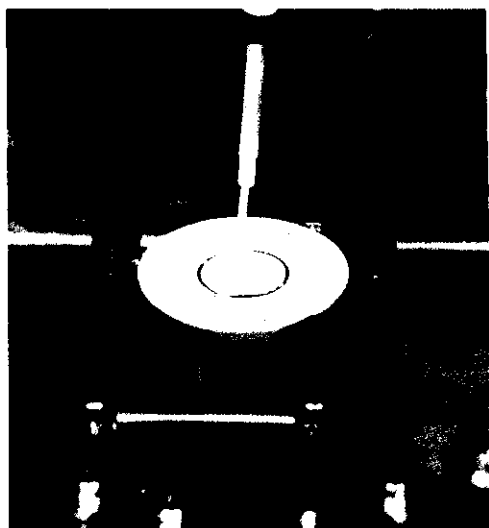Fig. 3 Filter paper used for microdroplet on-line electrolyte solution analysis

Photo 2 Dropping solution onto filter paper

balanced filter technique[3] or a semiconductor detector[8]. Abe et al.[9] and Yasui et al.[10] applied a second method, proposed by Murata et al.[11], in Kawasaki's electrogalvanizing lines. In this method the electrolyte solution on a filter paper is analyzed with a vacuum type fluorecent X-ray analyzer to analyze metallic elements and the light elements added to the electrolyte as supporting agents and contained in phosphating solutions. A constant volume $(60\,\mu l)$ of diluted solution (1:20) is dropped onto the filter paper and dispersed uniformly. To avoid spreading of the electrolyte, the analytical area of the filter paper is separated by a 1 mm gap and four supporting bridges which are soaked with paraffin (Fig. 3 and Photo 2). After drying, the filter paper is analyzed with a vacuum type X-ray fluorescence spectrometer. The sampling system is shown in Fig. 4. Analysis in a vacuum makes possible the precise analysis of light elements. Correction for the inter-element effect of light and heavy elements improves the
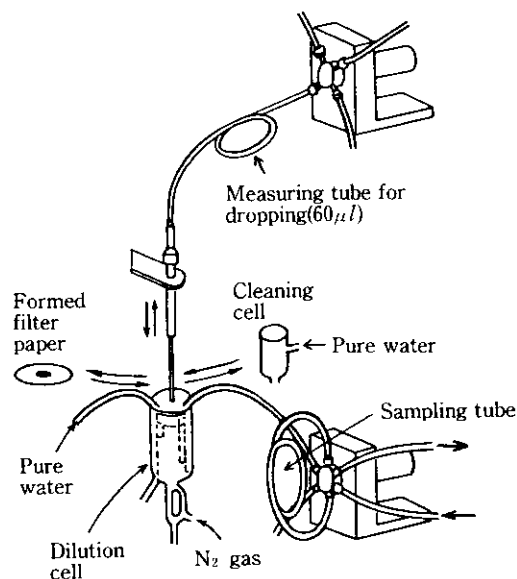

Fig. 4 Sampling-dilution-dropping system used for on-line electrolyte solution analysis

accuracy of this technique, which is 0.80 g/l for Zn and 0.16 g/l for Ni with correction.

This section mainly describes analysis techniques for the Zn-Ni alloy electrolytes. However, it may be noted that the same techniques can be applied to Zn-Fe alloy electrolytes and other solutions (used for zinc phosphate and chromate treatments).

3 Analysis Method for Zn-Fe Electroplated Coatings and Fe-P/Zn-Fe Double-Layer Coatings

In the analysis of a Zn-Fe alloy coating, it is necessary to distinguish the Fe in the coating from the Fe of the base steel. Fujino et al.[12] proposed an X-ray fluorescence method with two incident and take-off angles, which utilizes differences in X-ray pass length with known X-ray absorption coefficient of the coating. By measuring Zn and Fe fluorescence X-ray intensities at different incident and take-off angles and solving simultaneous equations, coating weights and Fe contents are obtained.

Yamamoto et al.[13] of Kawasaki Steel developed an on-line analysis method for Zn-Fe alloys using X-ray diffraction and X-ray fluorescence techniques. It was found that the lattice parameters of the Zn-Fe intermetallic compounds electroplated from a chloride bath vary with Fe content, which is determined by measuring the X-ray diffraction angle of a specific lattice plane (Fig. 5).

Based on this method of Zn-Fe analysis, Yamamoto et al. then developed an on-line analysis method[13] for Fe-P/Zn-Fe double-layer electroplated steel[14], in which it is possible to analyze the Fe-P coating weight, Zn-Fe coating weight, and Fe content of the Zn-Fe coating simultaneously, as shown in Fig. 6. Intensities of the
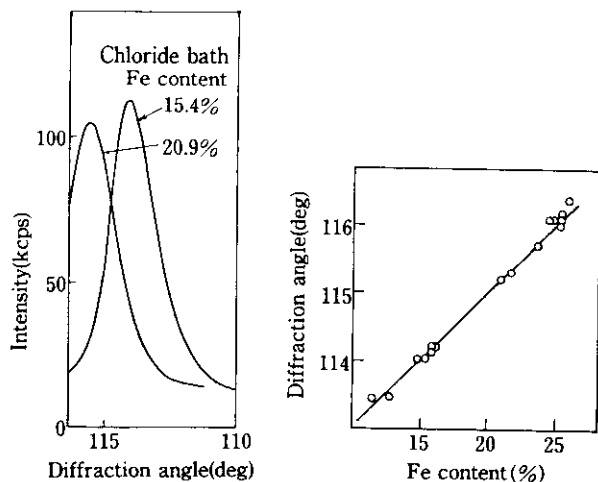
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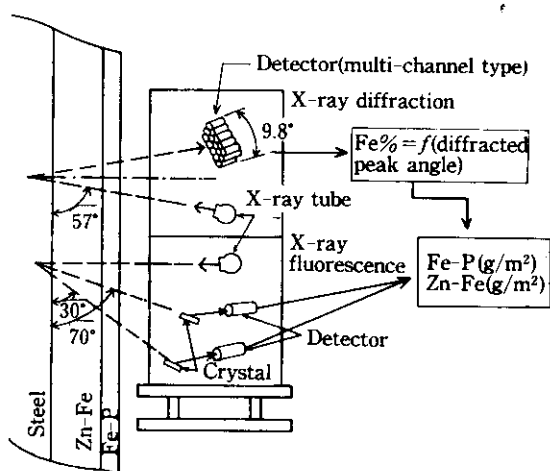Fig. 5 Shifts of diffracted X-ray peak position with Fe% in Zn-Fe alloy

Fig. 6 Analysis method for Fe-P/Zn-Fe electroplated steel sheet

Zn fluorescent X-ray from the Zn-Fe coating can be theoretically expressed by Eq. (1).

$$I_{Zn}^{\theta} = KI_0 W_{Zn} \exp\left\{-T_2\left(\frac{\mu_2^{\lambda}}{\sin\psi} + \frac{\mu_2^{ZnK\alpha}}{\sin\theta}\right)\right\}$$

$$\times \left[1 - \exp\left\{-T_1\left(\frac{\mu_1^{\lambda}}{\sin\psi} + \frac{\mu_1^{ZnK\alpha}}{\sin\theta}\right)\right\}\right]$$

$$\times \frac{1}{(\mu_1^{\lambda}/\sin\psi) + (\mu_1^{ZnK\alpha}/\sin\theta)}\right] \cdot (1)$$

where I_{Zn}^{θ}: Zn fluorescent X-ray intensity at take-off angle θ

I_0: Intensity of incident X-ray

θ: Take-off angle

ψ: Incident angle

$\mu_1^{ZnK\alpha}, \mu_2^{ZnK\alpha}$: Mass absorption coefficient of Zn-Fe and Fe-P coating at Zn $K\alpha$ line

$\mu_1^{\lambda}, \mu_2^{\lambda}$: Mass absorption coefficient of Zn-Fe and Fe-P coating at incident X-ray

K: Constant

T_1: Zn-Fe coating weight

T_2: Fe-P coating weight

W_{Zn}: Zn content $(1 - W_{Fe})$

An approximation of Eq. (1), obtained by expanding the equation and disregarding the high order series, gives Eq. (2).

$$I_{Zn}^{\theta} = aW_{Zn}T_1 + bW_{Zn}T_1^2 + cW_{Zn}^2T_1^2 + dW_{Zn}T_1T_2$$
$$+ eW_{Zn}T_1^2T_2 + fW_{Zn}^2T_1^2T_2 + g \cdots (2)$$

where $a \sim g$: constant

The unknown values in the Eq. (2) thus derived are the two coating weights and Fe content, which is determined by X-ray diffraction analysis. The remaining two unknowns are then calculated by measuring the Zn fluorescent X-ray intensities at two different take-off angles (30° and 70°) and solving simultaneous equations.

This method is in practical use, and shows an accuracy of 0.23 g/m² for the Fe-P alloy coating weight, 0.59 g/m² for the Zn-Fe coating weight, and 0.16% for Fe content. In order to conduct an analysis of sufficient speed for the on-line use, a multi-channel detector is used in the X-ray diffraction analysis. The incident angle of X-rays is set at 57° in order to measure the peak close at 114°. The obtained results with this method agreed with those measured by a goniometer. In the X-ray fluorescence analysis, the incident angle is set at 90° to reduce errors produced by fluctuation of the strip pass line.

4 On-line Analysis of Degree of Alloying in Galvannealed Coating

Galvannealed coatings are produced by heating the strip after hot dip type Zn coating to obtain an inter-diffused Zn-Fe alloy. The alloy consists of ζ phase ($FeZn_{13}$), δ_1 phase ($FeZn_7$), and Γ (and/or Γ_1) phase (Fe_5Zn_{21}). In comparison with pure Zn coated steel, galvannealed steel sheet is known to show better corrosion resistance after painting, spot weldability, and paint adhesion. However, as galvannealing proceeds, the amount of Fe-rich phase components, such as the Γ and/or Γ_1 phases, increases with the diffusion process, causing deterioration of coating ductility and adhesion and leading to "powdering," a partial coating separation during press forming or bend forming[15]. Therefore, the allowable ranges of Fe% and/or amounts of the various coating phases are limited.

Because the phases of galvannealed coatings are different from those of electroplated steel and the surface roughness of galvannealed steel is greater than that of electroplated, the techniques used for Zn-Fe alloy electroplated steels cannot be applied to galvannealed products. Proposed techniques include quantitative analyses
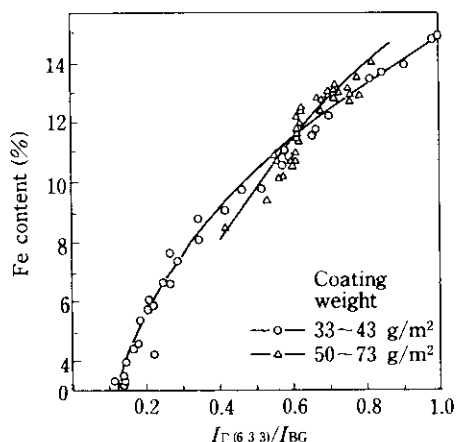
Fig. 7 Relation between Fe content and diffracted X-ray peak intensity

Fig. 8 Phase composition of galvannealed coating[17]

of various coating phases by the X-ray diffraction method[16,17] and laser-based surface roughness analysis[18].

Ito et al.[16] developed an on-line analytical technique to measure the degree of alloying in galvannealed coatings by using a Z value which is a ratio of the diffracted X-ray intensity of the ζ-phase to the δ_1-phase $(Z = I(\zeta)/I(\delta_1))$.

Kawabe et al.[17] of Kawasaki Steel developed and put into practical use an X-ray diffraction method for the continuous analysis of Fe content in the coating and coating weight. By studying various peaks of diffracted X-rays from the coating, they found that the intensity ratio of a diffracted X-ray peak, with background correction, from Γ (6 3 3) and/or Γ_1 (12 6 6) at $2\theta = 139°$ (by a Cr target) to the background relates to the Fe content of the coating. This relation holds when the coating weight is constant and the Fe content is from 3 to 15%, as shown in **Fig. 7**. By using these relations, the Fe content is determined. Using this Fe content and measured Zn fluorescent X-ray intensities, coating weight is calculated.

Although this method is used practically, it should be noticed that significant amounts of Γ and/or Γ_1 phases are not present in the coating when the Fe content is below 12%. It is reported[19,20] that below 12% the main phase is δ_1, and a ζ phase appears when the Fe content is below 8% (**Fig. 8**). Recently, Katayama et al.[21] found that a δ_1 phase (5 5 14) has a peak at $2\theta = 139°$. Therefore, the diffracted X-ray peak at 139° used in this analysis can be understood as consisting mainly of diffracted X-rays from the δ_1 phase when the Fe content is below 12%, as shown in **Fig. 9**.

As instrumentation, a parallel beam diffractometer is used with a broad-focus Cr target X-ray tube (3 kW) operated at high power (70 mA-40 kV: filament current-voltage) to obtain strongly diffracted X-rays (**Fig. 10** and **Photo 3**). The X-ray intensities are measured at 139.0° for the δ_1 (5 5 14), Γ phase (6 3 3) and/or Γ_1 phase
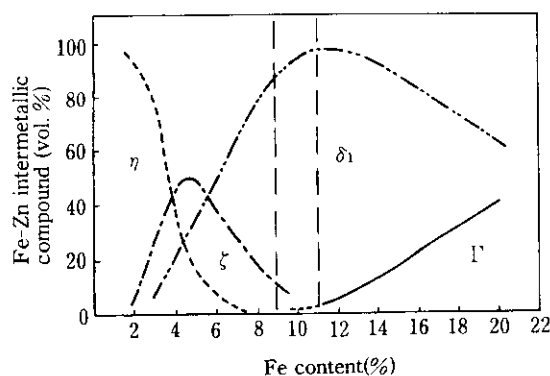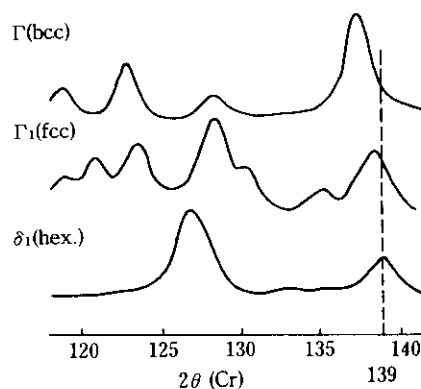

Fig. 9 X-ray diffraction patterns of galvannealed coating

① Background 90°
② Γ (633) 139°
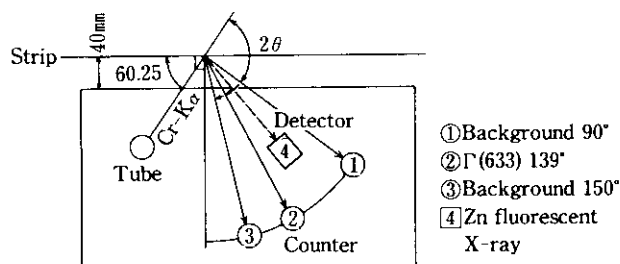③ Background 150°
④ Zn fluorescent X-ray

Fig. 10 Analysis method for galvannealed coating by X-ray diffraction combined with X-ray fluorescence

(12 6 6), and 90.0° and 150.0° for the background. The analytical accuracy of this method is 0.6% for Fe content and 2.5 g/m² for coating weight.

5 Further Developments

Demand for precise, sophisticated methods of on-line analysis is likely to increase further due to the strictness of quality requirements for Zn alloys and the need for reliable quality control in continuous, high-speed operation. The development of on-line analysis has to date

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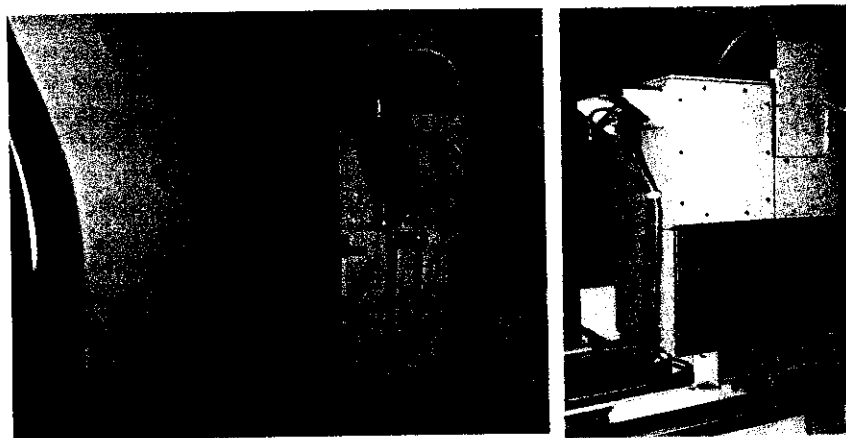
(a) Back side   (b) Front side

Photo 3   Measuring head of Fe content analyzer

concentrated on the analysis of coating weight and alloy content, which represent average and/or total information on the coating. With the on-line analysis method developed by Kawabe et al., it is possible to determine the average Fe content of the whole coating[17], but this does not specify the phase composition. However, as discussed in Sec. 4, the qualities of galvannealed steel sheet change with phase composition. As for press formability, for example, the Γ phase causes deterioration of the antipowdering property[15], while the ζ phase increases frictional resistance, which leads to splitting in steel panels[22]. Even when the analysis value of the Fe content is constant, the phase composition may vary with substrate steel compositions and galvannealing conditions[15]. Therefore, it is highly desirable that a method be developed for the quantitative on-line analysis of each phase of galvannealed coatings.

In addition, a new coating in which a thin Fe-P[22] or Fe-Zn alloy layer is electroplated over a galvannealed coating has been developed and is now in commercial application. As with the Fe-P layer on the electroplated Zn-Fe alloy, coating weight measurements of this layer are important and may be conducted with a combined method for Fe-P/Zn-Fe coating analysis and galvannealed coating analysis. However, due to Fe content variations in the depth direction of galvannealed coatings, the accuracy of this method is poor. Thus, development of a new method to measure the Fe-P top layer coating weight is also strongly required.

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