On-line Analyzer for Ni–Zn Alloy Electroplated Coating on Steel

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The Ni–Zn electroplated steel sheet is used as a car body material because of its high corrosion resistance. On production of this sheet, the coating weight and Ni content of the alloy coating are necessary to be controlled within limited ranges to ensure the quality of the products. An on-line X-ray fluorescence analyzer has been developed for the determination of the coating weight and Ni content of the alloy coating. The features of the analyzer are summarized as follows:

1) The analysis is carried out full automatically.
2) X-ray intensities are measured by a detector (ionization chamber) with an Fe filter and the other with a Ni filter.
3) The coating weight and the Ni content are calculated from the intensities measured by the two detectors.

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1. Introduction

Ni–Zn alloy electroplated steel sheets have been developed as autobody materials with high corrosion resistance.1) The coating weight and Ni content of the coating are necessary to be controlled within limited ranges to ensure the quality of sheets. Coatings are often analyzed by the X-ray fluorescence analysis method because of easy operation and rapid response. It has already been applied to the analysis of zinc and tin coatings on steel sheets. The on-line ("noninvasive" as defined by Callis et al.2) analysis techniques of the zinc coating weight in continuous galvanizing lines3) and the tin coating weight in tin coating lines4) have been developed. However, the on-line analysis of both coating weight and composition of alloy coatings has been hardly carried out. From these backgrounds, an on-line X-ray fluorescence analyzer for the Ni–Zn alloy electroplated coating has been developed. In the on-line analyzer, an energy discrimination method with filters has been devised. The method has made it possible to determine both coating weight and composition from the intensities measured by a detector with an Fe filter and the other with a Ni filter.

Moreover, Cu–Zn plating films5,9) on steel were also analyzed by using the line intensities of the coating and substrate elements. The on-line analysis of the Ni–Zn alloy electroplated coating has been developed based on the following results. The principle of coating thickness measurement by X-ray fluorescence is applied to the present analysis of Ni–Zn alloy coatings. Fig. 1 shows the schematic diagram of fluorescent X-rays emitted from a Ni–Zn alloy plated steel. The equations for primary fluorescent Ni, Zn, and FeKα X-ray intensity for monochromatic excitation are:

\[
I_{N\alpha K\alpha} = \frac{k_{N\alpha} \cdot I_{K\alpha}}{\sin \phi} \cdot \frac{W_{N\alpha}[1 - \exp \{-\phi \cdot W_{N\alpha} + \phi \cdot W_{Zn} \cdot \phi\}]}{\phi \cdot W_{N\alpha} + \phi \cdot W_{Zn}}
\]

\[
\mu_{N\alpha} \cdot \mu_{K\alpha} = \frac{k_{N\alpha} \cdot I_{K\alpha}}{\sin \phi} \cdot \frac{W_{Zn}[1 - \exp \{-\phi \cdot W_{N\alpha} + \phi \cdot W_{Zn} \cdot \phi\}]}{\phi \cdot W_{N\alpha} + \phi \cdot W_{Zn}}
\]

\[
I_{ZnK\alpha} = \frac{k_{Zn} \cdot I_{K\alpha}}{\sin \phi} \cdot \frac{\exp \{-\phi \cdot W_{N\alpha} + \phi \cdot W_{Zn} \cdot \phi\}}{\phi \cdot W_{N\alpha} + \phi \cdot W_{Zn}}
\]

where, \( k_{N\alpha}, k_{Zn}, k_{K\alpha} \) : Constants

2. Principle of X-ray Fluorescence Analysis

The thickness and composition of alloy coatings can be determined from the intensities of characteristic emission lines from coating and/or substrate elements. It has been already made clear that Fe–Ni films8,9) and Pb–Sn coatings10) can be analyzed by measuring the emitted line intensities of alloy coating elements.
Fig. 1. Schematic diagram of fluorescent X-rays emitted from a Ni-Zn alloy plated steel.

\[ I_{NIK\alpha}, I_{ZNK\alpha}, I_{FeK\alpha} \]: Intensities of NiK\alpha, ZnK\alpha and FeK\alpha lines, respectively

\[ I_0 \]: Intensity of incident X-rays

\[ \delta \]: Thickness of Ni-Zn alloy coating

\[ W_{NI}, W_{ZN} \]: Ni and Zn contents in alloy coating, respectively

\[ \rho_{NI}, \rho_{ZN} \]: Mass absorption coefficients of element \( j \) (Ni and Zn) and Fe (substrate element) for incident X-rays (wavelength of \( \lambda \)), respectively

\[ \rho_{Ni}^{NIK\alpha}, \rho_{Zn}^{NIK\alpha} \]: Mass absorption coefficients of element Ni and Zn for NiK\alpha and ZnK\alpha lines, respectively

\[ \rho_{Fe}^{FeK\alpha} \]: Mass absorption coefficient of element Fe for FeK\alpha line, respectively

\[ \rho, \phi, \psi \]: Density of Ni-Zn alloy coating, Incidence and takeoff angles, respectively.

The determination procedure of coating weight was studied. In the Ni content range of about 10 to 16 %, the NiK\alpha line intensity varies largely with Ni content, as understood from Eq. (1). For this reason, the coating weight is difficult to be determined from the NiK\alpha intensity. For the same reason, the coating weight can not be determined from the ZnK\alpha intensity alone. On the other hand, the intensity of the FeK\alpha line varies exponentially with Ni content as understood from Eq. (3). The FeK\alpha line intensity was calculated as functions of coating weight and Ni percentage. Table 1 shows the mass absorption coefficients\(^{18,19}\) used for the calculation. The incident X-rays were of a monochromatic beam of wavelength of 8 Å, and \( \phi \) and \( \phi \) were 60° and 35°, respectively. Fig. 2 shows the calculation results. The coating weight can be determined from a single calibration curve (FeK\alpha line intensity vs. coating weight) in the Ni content range of about 10 to 16 %. Although the calculated data for Ni content determination are not shown in the present paper, the results are summarized as follows: the intensities of the NiK\alpha and ZnK\alpha lines at a constant Ni % vary largely with coating weight.

The above calculation results were experimentally confirmed with a wavelength-dispersive X-ray fluorescence spectrometer. The reference samples used for the experiments were prepared in the following manner. The Ni-Zn alloy was electroplated in a plating bath of nickel sulfate and zinc sulfate. The substrate was a cold rolled steel sheet. The Ni-Zn alloy coating of each sample was dissolved in a mixture of HCl and H\textsubscript{2}O\textsubscript{2}. The coating weights were determined by the gravimetric (weigh-strip-weigh) method. The contents of Ni and Zn were determined by atomic absorption spectrometry. The concentrations of Ni and Zn in the dissolved solution were converted to the Ni content of the alloy coatings. The specimens for X-ray fluorescence analysis were cut just near the chemically analyzed points. Good correlation between the FeK\alpha line intensity and the coating weight is obtained, as shown in Fig. 3. Fig. 4 shows the relationship between the NiK\alpha line intensity and the Ni %. The NiK\alpha line intensity increases with increasing coating weight. The coating weight can not be determined from the NiK\alpha line intensity without correction of the coating weight.

Types of detectors suitable for on-line analysis are considered. For on-line analysis, an energy-dispersive proportional counter and an ionization chamber with filters\(^{20}\) are often used. An energy-dispersive method with a Si (Li) solid state detector and a wavelength-dispersive method with an analyzing crystal can be also adopted. A proportional counter has an energy resolution to separate the Fe and Zn K lines emitted from Zn coated steel. Therefore, the counter has been used for the Zn coating weight measurement of Zn coated steel sheets.\(^{21}\) However, the energy resolution of proportional counter is not enough to detect separately the Fe, Ni and Zn K lines emitted from Ni-Zn coated steel. From these reasons, an energy discrimination method with filters\(^{22}\) was studied. The intensity of the Fe line is measured by using an
ionization chamber with an Fe filter. The intensities of the Ni and Fe lines are measured by means of an ionization chamber with a Ni filter. The coating weight and composition are obtained from these measured intensities.

3. Measuring Method in On-line Analyzer

The measuring methods are summarized as follows:

(1) When characteristic X-rays of Fe, Ni and Zn elements emitted from a Ni-Zn electroplated steel sheet pass through an Fe filter, the intensities of the Ni and Zn lines decrease more than that of the Fe line. The coating weight is determined from the intensity measured with an Fe filtered detector by using Eq. (5) as will be described later.

(2) When fluorescent X-rays emitted from a Ni-Zn electroplated steel sheet transmit a Ni filter, the X-rays of the Zn line are absorbed more by the filter than those of the Ni and Fe lines. The intensities were converted to the Ni content by using Eq. (15).

The absorbances of Fe and Ni filters for emitted lines from Ni-Zn alloy coating were theoretically evaluated. In the calculation mass absorption coefficients tabulated by Liebhafsky et al. were used. The values for FeKα and Kβ, NiKα and Kβ and ZnKα and Kβ lines were obtained by interpolation. The Kα and Kβ line intensities are difficult to be detected separately because of the poor resolution of the detector instrument. Therefore, the intensities of the Kα and Kβ lines were represented as that of the K line. The intensity of X-rays transmitted through a filter, I, was calculated from Eq. (4).

\[ I = I_0^s \cdot e^{-\mu_{Kα} \cdot \rho_{F} \cdot t_{F}} + I_0^s \cdot e^{-\mu_{Kβ} \cdot \rho_{F} \cdot t_{F}} \]

where, \( I_0^s \): Incident X-ray intensity of K line (Kα and Kβ lines are not resolved),
\( \mu_{Kα}, \mu_{Kβ} \): Mass absorption coefficients of a filter for Kα, Kβ and K lines, respectively
\( \rho_{F}, t_{F} \): Density and thickness of filter, respectively.

The ratio of the Kα to the Kβ line intensities, \( I_0^s: I_0^s = 150:20 \), was used in calculation. The intensities of X-rays of the Ni, Zn and Fe lines passed through Fe and Ni filters were calculated and the results are shown in Figs. 5 and 6. The fluorescent X-rays of the Ni and Zn lines are more absorbed by Fe filters than those of the Fe line. The intensity measured by the detector with a 20 μm thick Fe filter is approximately equal to that of the Fe line. The fluorescent X-rays of the Zn element line are more absorbed by a Ni filter than those of the Fe and Ni element lines. The intensity measured by the detector with a 20 μm thick Ni filter is approximately equal to the sum of the intensities of the Fe and Ni lines. The coating weight can be determined from the intensity measured by the Fe filtered detector. The intensity equation is given by Eq. (3).

\[ N_{Fe} = \frac{k_{Fe} \cdot I_0}{\sin \phi \cdot (e^{-\mu_{Fe} \cdot \rho_{F} \cdot t_{F}} + e^{-\mu_{Fe} \cdot \rho_{F} \cdot t_{F}})} \]

where, \( k_{Fe} \): Constant
\( I_0 \): Incident X-ray intensity
\( N_{Fe} \): Measured X-ray intensity detected by a detector with a 20 μm thick Fe filter
\( \mu_{Fe} \): Mass absorption coefficients of Fe for incident X-ray (wavelength of \( \lambda \)) and FeK line, respectively
\( \mu_{Ni-Zn} \): Mass absorption coefficients of Ni-Zn alloy for incident X-ray.
$P_{FeK}^n$, $P_{NiK}^n$, $P_{ZnK}^n$: Intensities of FeK, NiK and ZnK lines emitted from a Ni-Zn alloy electroplated steel sheet, respectively.

Eqs. (6) and (7) are approximated by Eqs. (8) and (9), on the basis of the calculation results in Figs. 5 and 6.

\[ N_{Ni} = 0.21P_{FeK}^n + 0.35P_{NiK}^n \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (8) \]

\[ N_{Fe} = 0.33P_{FeK}^n \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (9) \]

The $N_{Ni}/N_{Fe}$ ratio is represented by

\[ N_{Ni}/N_{Fe} = k + k' \cdot (P_{ZnK}^n/P_{FeK}^n) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (10) \]

$I_{FeK}^0$ and $I_{NiK}^0$ are given by

\[ I_{FeK}^0 = \frac{k_{Fe} \cdot I_{0} \cdot W_{Ni}}{\sin \phi} \cdot \left[ 1 - \exp \left\{ - \left( \frac{\mu_{Fe}^n \cdot \sin \phi + \mu_{FeK}^n \cdot \sin \phi}{\sin \phi} \right) \cdot t \right\} \right] \frac{\mu_{Fe}^{nK} + \mu_{Fe}^{nK} \cdot \sin \phi}{\sin \phi} \cdot \left( \frac{1}{\sin \phi} + \frac{\mu_{Fe}^{nK} \cdot \sin \phi}{\sin \phi} \right) \cdot t \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (11) \]

\[ I_{NiK}^0 = \frac{k_{Ni} \cdot I_{0} \cdot W_{Ni}}{\sin \phi} \cdot \left[ 1 - \exp \left\{ - \left( \frac{\mu_{Ni} \cdot \sin \phi + \mu_{NiK} \cdot \sin \phi}{\sin \phi} \right) \cdot t \right\} \right] \frac{\mu_{Ni}^{nK} + \mu_{NiK}^{nK} \cdot \sin \phi}{\sin \phi} \cdot \left( \frac{1}{\sin \phi} + \frac{\mu_{Ni}^{nK} \cdot \sin \phi}{\sin \phi} \right) \cdot t \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (12) \]

where, \( \mu_{NiK}^{nK} \): Mass absorption coefficient of Ni-Zn alloy for NiK line.

The intensity ratio $I_{FeK}^0/I_{NiK}^0$ is represented by the Taylor expansion and approximation as

\[ \frac{I_{NiK}^0}{I_{FeK}^0} = \frac{k_{Ni} \cdot W_{Ni} + \mu_{Fe}^{nK} \cdot \sin \phi}{k_{Fe} \cdot W_{Ni} + \mu_{Ni}^{nK} \cdot \sin \phi} \cdot t \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (13) \]

by using the relations,

\[ \mu_{Ni}^{nK} = \mu_{Ni} \cdot W_{Ni} + (1 - W_{Ni}) \cdot \mu_{Zn} \]
\[ \mu_{Fe}^{nK} = \mu_{Fe} \cdot W_{Fe} + (1 - W_{Fe}) \cdot \mu_{Zn} \]
\[ \mu_{Ni-Zn}^{nK} = \mu_{Ni} \cdot W_{Ni} + (1 - W_{Ni}) \cdot \mu_{Zn} \]

where, \( \mu_{Fe}, \mu_{Ni}, \mu_{Zn} \): Mass absorption coefficients of Fe, Ni and Zn for incident X-rays (wavelength of $\lambda$), respectively

\( P_{FeK}^n, P_{NiK}^n, P_{ZnK}^n \): Mass absorption coefficients of FeK, NiK and ZnK lines, respectively

\( k_{Fe}, k_{Ni}, k_{Zn} \): Mass absorption coefficients of FeK, NiK and ZnK lines, respectively

\( k_{Ni} = k_{Fe} = k_{Zn} = \) Constants.

The $N_{Ni}/N_{Fe}$ ratio is represented by Eq. (14) from Eqs. (10) and (13).

\[ \frac{N_{Ni}}{N_{Fe}} = k_{0} + k_{1} \cdot W_{Ni} \cdot \rho \cdot t + k_{2} \cdot W_{Ni} \cdot (\rho \cdot t)^{2} + k_{3} \cdot (W_{Ni} \cdot \rho \cdot t)^{3} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (14) \]
where, \( k_s, k_1, k_2, k_3 \): Constants.
Moreover, the \( \frac{N_{ni}}{N_{py}} \) ratio is given by

\[
N_{ni} = k_{0} + k_{1}\cdot x_{ni} + k_{2}\cdot x_{ni}^{2} + k_{3}\cdot x_{ni}^{3}
\]

(15)

where, \( x \): Total coating weight
\( x_{ni} \): Coating weight of Ni in a unit area (\( x_{ni} = \omega_{ni}\cdot x \)).
The coating weight and Ni % of the coating were determined from Eqs. (5) and (15).

4. Outline and Capabilities of On-line Analyzer

4.1. Outline

The schematic diagrams of the X-ray fluorescence measurement system, and the traversing stand and measuring heads are shown in Figs. 7 and 8. The electroplated strip passes the measuring heads. The measurement system composes of the measuring heads, electronics units, an I/O (interface), and a computer. The coating weight and Ni content are simultaneously determined from the X-ray fluorescence intensities detected by the measuring heads. The upper and lower limits for coating weight and Ni content designed for production control are input to the computer. If an analytical value deviates from the limited values, the computer outputs an alarm signal. One measuring head consists of an X-ray tube and two detectors. The incidence and takeoff angles are 45° and 80°, respectively. A tungsten target X-ray tube is used for higher excitation efficiency and operated at 30 kV–140 \( \mu \)A.

Reference samples used for obtaining calibration equation constants can be set at the sample holder. The measuring heads are moved to the sample holder position and the intensities of the samples are measured. The constants of the calibration equations are calculated from the measured intensities. The X-ray intensity of each sample was measured before the installation of the analyzer in the plant. The intensities of calibration samples can be also measured after the installation of the analyzer on the production line. In the production line the reference sample were replaced by three samples of a zinc sheet, a steel sheet and an 18–8 stainless steel sheet for instrument drift correction. The sample size is 150 mm \( \times \) 120 mm and X-ray measuring area is about 50 \( \times \) 50 mm\(^2\). The correction equations are given by

\[
N_{ni}^{\prime} = a\cdot N_{ni} + b
\]

(16)

\[
N_{ni}^{\prime} = a'\cdot N_{ni}^{\prime} + b'
\]

(17)

where, \( N_{ni}, N_{ni}^{\prime} \): Intensity measured by a detector with a 20 \( \mu \)m thick Fe filter and that with a 20 \( \mu \)m thick Ni filter, respectively, in preparing calibration equations

\( N_{ni}^{\prime}, N_{ni}^{\prime} \): Measured intensities for drift correction

\( a, b, a', b' \): Constants.

Three reference samples are measured by each detector of the upper and lower measuring heads. In on-line analysis the drift is corrected every 8 h.

The measuring heads are operated in three kinds of measuring modes as shown in Fig. 9. The scanning measuring mode analyzes coatings in the traversed direction at a scanning speed of 25 mm/s.

The three-point-measuring-mode analyzes the center and two edge sides of the steel sheet alternately. The analysis time at each position is 4 s. The one-point-measuring-mode analyzes a selected steel sheet position continuously. The following operations are made with a control panel: display and recording of

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**Fig. 7.**
Schematic diagram of the X-ray fluorescence measurement system.

**Fig. 8.**
Schematic diagram of traversing stand and measuring heads.
analytical values; input of upper and lower limits; and choice of measuring mode.

Experimental results by the on-line analyzer are shown below. Fig. 10 shows the relationship between the X-ray intensity measured by the detector with a 20 μm thick Fe filter, \( N_{Fe} \), and the coating weight. The relation was represented as a single working curve with little influence of Ni content. The ratio, \( N_{Ni}/N_{Fe} \), had a good relationship with Ni coating weight in a unit area for a group of nearly constant coating weight, as shown in Fig. 11. The coating weight and Ni content of each sample in these calibration curves were determined from each intensity by using Eqs. (3) and (15). These determined values were compared with the chemical analysis values. X-ray and chemical analysis values for coating weight and Ni content are compared in Figs. 12 and 13, respectively. The X-ray analytical values agreed well with the chemical analysis values.

The analytical accuracies, \( \sigma_d = \sqrt{\sum p^2/(n-1)} \), \( d = (\text{X-ray fluorescence analysis value}) - (\text{Chemical analysis value}) \), (number of samples), of coating weight and Ni content were 0.23 g/m² and 0.55 %, respectively. These values indicate that the on-line analyzer can be used for process operation.

4.2. Factors Affecting Analytical Values

Analytical values are affected by many factors such as temperature, the distance between the measuring head and the strip surface, twisting of steel sheets,
etc. The influence of atmospheric temperature on analytical values was examined as shown in Fig. 14. Changes of atmospheric temperature in the gap between a strip surface and a detector cause changes in absorption of X-rays, characteristics of electronics unit, etc. In on-line analysis, the intensity change is compensated by measuring reference samples. Analytical values also vary due to the change in the distance between the measuring head and the strip surface as shown in Fig. 15. The distance between the measuring head and the strip surface, the air gap, is normally 42 mm. Changes of ±2 mm in the gap resulted in an increase of coating weight by 0.2 to 0.3 g/m², and a decrease of Ni content value in the range of 0.1 to 0.2 % due to the decrease of the \( N_{Fe} \) and \( N_{Ni} \) intensities. The influence of steel sheet twisting was as follows. Variations of ±1° in the angle between the measuring head and the line direction strip surface, \( \alpha \), resulted in variations of less than ±0.05 g/m² coating weight and ±0.1 % Ni content values. Variations of ±1° in the angle between the measuring head and the transversal direction strip surface, \( \beta \), caused the variation of about ±1 g/m² coating weight, and about ±1 % Ni content values. The on-line analyzer was installed in a suitable position of the coating line to avoid these affecting factors.

4.3. **On-line Analysis Results**

On-line X-ray fluorescence analysis values were compared with off-line chemical analysis values performed in the following way: When a measuring point on a plating steel sheet passed the on-line analyzer head, the measuring point was marked and the X-ray fluorescence analysis values were simultaneously recorded. A specimen was cut from the marked point for chemical analysis. Fifteen coils were examined. Fig. 16 shows the results of coating weight. The on-line analysis values agreed well with the off-line values. A satisfactory analytical accuracy, 0.77 g/m², was obtained. Fig. 17 shows the results of Ni content. The on-line analysis values agreed well with the off-line analysis values. A good analytical accuracy, 0.89 %, was also obtained. This on-line analyzer has been applied to the analysis of Zn electroplated steel sheets. It has been operated for seven years without any trouble.

5. **Conclusions**

An on-line analyzer has been developed for the determination of the coating weight and Ni content of the Ni–Zn alloy electroplated steel sheets. The features of the analyzer are summarized as follows:

1. The analysis is automatically and continuously carried out on a production line.
2. The X-ray fluorescence analysis method by the energy discrimination technique with filters was adopted. The coating weight and the Ni content are calculated from the intensities measured by two de-
tectors with an Fe filter and with a Ni filter.

3) Good on-line analysis accuracies were obtained: 0.77 g/m² for coating weight and 0.89 % for Ni content.

4) This on-line analyzer has been also applied to zinc electroplated steel sheets and has been operated for seven years without any trouble.

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