X-ray Fluorescence Analysis of Alloy-electroplated Coatings on Steel with K and L Series Emissions

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Synopsis

The Fe-Zn and Ni-Zn alloy electroplated coatings were analyzed by the X-ray fluorescence spectrometric method. The critical thickness for an L series line is less than for a K series. The thickness of the common coating is greater than the critical thickness for the L series line and smaller than that for the K series. The composition of the coating was determined only from the ZnLa line intensity. The coating weight was determined from the K series line intensity and the composition which was obtained from the ZnLa line intensity.

Key words: electroplating; alloy coating; X-ray fluorescence analysis; coating weight; coating composition.

I. Introduction

Various kinds of high corrosion-resistant alloy-electroplated steel sheets have been developed.1)2) The coating weight and composition of alloy coatings are important parameters of the alloy-electroplated steel sheets. The X-ray fluorescence spectrometric method is often used for the analysis of coatings.3)7) In the X-ray fluorescence analysis of alloy electroplated coatings, the fluorescent X-ray intensity is generally a function of the coating weight (coating thickness) and the coating composition. For the analysis of coatings the fluorescent X-ray intensities of coating8)10) or substrate elements11)12) are used. However, it is difficult to analyze Fe-Zn alloy electroplated steel sheets by the conventional X-ray fluorescence analysis method because both the coating and the substrate contain iron. The coatings composed of elements from Cr (Z=24) to Zn (Z=30) were analyzed with K series fluorescent X-rays.

In this study the X-ray fluorescence analysis with low-energy X-rays of about 3 to 20 A wavelengths13)26) the L series X-rays of the coating element, was applied to the analysis of the Fe-Zn and Ni-Zn alloy coatings. On the fluorescence analysis with low-energy X-rays, the studies of measurements of mass absorption coefficients, apparatuses, determination of Na and F contents in cements15)24) have been reported. The thicknesses of the oxide films which contain the substrate element, e.g., SiO2 on Si,25) FeO/FecO4 on Fe,26) TiO2 on Ti,26) have been determined. However, no study on the determination of the composition of such alloy coatings have been reported.

This report describes the research results of the X-ray fluorescence analysis of Fe-Zn and Ni-Zn alloy coatings with the K and L series emissions. The L series fluorescent X-rays are absorbed by coatings more than the K series X-rays. The intensity of the L series line for coating of ordinary thickness is a function of the coating composition. The composition of Fe–Zn alloy coating was determined from the L series fluorescent X-ray (ZnLa line) intensity. The coating weight was determined from the K series fluorescent X-ray intensity and the above determined composition value. Coatings of Ni–Zn alloy coating were also analyzed.

II. Principle

The fluorescent X-ray intensities of coating and substrate elements are a function of the coating weight and composition of alloy coatings as shown below. The coating weight means the weight on a unit area and the term “coating weight” is frequently used in the field of X-ray fluorescence spectrometric method to represent the measurement between opposite surfaces of a coating. However, the weight on a unit area (p·t, p: density, t: thickness) is measured by X-ray fluorescence analysis. It is convenient to use “coating weight” when the density varies with the coating composition. “Coating weight” is often used in steel industries.

For these reasons, both “coating weight” and “coating weight” are used in the present paper. The fluorescent X-ray intensities of alloy coating elements are a function of the coating composition when the thickness is larger than a critical thickness.10)27) This critical thickness depends on analytical conditions: wavelength and incidence angle of incident X-rays, takeoff angle of fluorescent X-rays, coating composition, detecting fluorescent X-rays (Kα, Kβ, Lα, ...), etc.

The intensities of the K series lines from Fe–Zn and Ni–Zn alloy coatings are a function of coating weight and composition for the usual coating weight range of about 20 to 40 g/m2. On the other hand, the critical thickness is smaller for the L series fluorescent X-rays. The coating weight was determined from the K series fluorescent X-ray intensity and the above determined composition value.

The primary fluorescent X-ray intensities were calculated27)28) in the case of a monochromatic excitation source. The intensities from the Fe–Zn alloy coatings were also analyzed.

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Electroplated steel sheet in Fig. 1 are given as

\[ \begin{align*}
I_{\text{ZnLa}} &= k_{\text{ZnLa}} \cdot I_0 \cdot W_{\text{Zn}} \\
&\quad \cdot \left[ 1 - \exp \left( -\left( \frac{\rho_{\text{Fe-Zn}}}{\sin \phi} + \frac{\rho_{\text{Zn}}}{\sin \phi} \right) t \right) \right]
\end{align*} \]

\[ \begin{align*}
I_{\text{FeLa}} &= k_{\text{FeLa}} \cdot I_0 \cdot W_{\text{Fe}} \\
&\quad \cdot \left[ 1 - \exp \left( -\left( \frac{\rho_{\text{Fe-Zn}}}{\sin \phi} + \frac{\rho_{\text{Fe}}}{\sin \phi} \right) t \right) \right]
\end{align*} \]

Equations (1) and (2) are for the La lines. The equations for the Ka lines are obtained by replacing the subscript, La, with Ka. The calculation results will be shown below for the ZnLa and Ka line intensities measured in the experiments.

Table 1 shows the mass absorption coefficients \(^{14,29}\) used for calculation. The effective film thicknesses \(t_{1/1000}\) at which the transmitted X-ray intensities \(I\) becomes a thousandth of the incident X-ray intensity \(I_0\) were calculated from the Lambert–Beer law (\(I = I_0 \cdot \exp (-\mu \cdot \rho \cdot t)\); \(\mu\): mass absorption coefficient, \(\rho\): density, and \(t\): thickness). The results are shown in Table 2. The ratios of the effective thicknesses for the La lines to those for the Ka lines were in the range from 1/29.2 to 1/36.7.

![Fig. 1. Fluorescent X-rays from Fe–Zn alloy electroplated steel sheet.](image-url)

Table 2. Calculation of effective film thicknesses. \((t_{1/1000} \text{ (um)})\)

<table>
<thead>
<tr>
<th>Line (Å)</th>
<th>FeLa</th>
<th>NiLa</th>
<th>ZnLa</th>
<th>FeKa</th>
<th>NiKa</th>
<th>ZnKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>17.6</td>
<td>14.6</td>
<td>12.3</td>
<td>1.94</td>
<td>1.66</td>
<td>1.44</td>
</tr>
<tr>
<td>Ni</td>
<td>7.245</td>
<td>1.801</td>
<td>10.900</td>
<td>88.6</td>
<td>56.5</td>
<td>297</td>
</tr>
<tr>
<td>Zn</td>
<td>3.424</td>
<td>2.237</td>
<td>1.520</td>
<td>117</td>
<td>74.6</td>
<td>49.1</td>
</tr>
</tbody>
</table>

In the present paper, the coating weight at the \(I/I_0\) ratio of 0.99 is called a critical coating weight \((\rho_{\text{Fe-Zn}} t)_C\). The values are shown in Fig. 2. The wavelength of the ZnLa line is shorter than those of the FeL\(_{\text{II}}\), L\(_{\text{III}}\), and L\(_{\text{IV}}\) absorption edges. The wavelength of the ZnKa line is shorter than that of the FeK absorption edge. The ZnLa and Ka line X-rays are more absorbed by Fe than by Zn. For these reasons, the critical coating weights decrease with increasing Fe %. The critical coating weights for the ZnLa and ZnKa lines were compared; 8.6 g/m\(^2\) for ZnLa and 150 g/m\(^2\) for ZnKa at 80 % Zn and 3.6 g/m\(^2\) for ZnLa and 92.1 g/m\(^2\) for ZnKa at 20 % Zn. The coating composition can be determined even at a small coating weight with ZnLa line.

Figure 3 gives the relationships between critical coating weights and Zn %. In the region over the critical coating weights for the ZnKa line, the intensities of both the ZnLa and ZnKa lines are a function of only Zn %, not of coating weight. For the sample in this region the composition can be determined, but the coating weight remains unknown.

In the region, the intensity of the ZnKa line is a function of Zn % only. The intensity of the ZnKa line is a function of the coating weight and Zn %. The coating composition can be determined from the intensity of the ZnLo line. The coating weight can be determined from both the intensity of the ZnLa line and the above determined composition value.
In the region, \( \varnothing \), the intensities of the ZnL\(_\alpha\) and ZnKa lines are functions of Zn \( \% \) and the coating weight. The coating weight and composition can be determined from the intensities of the ZnL\(_\alpha\) and ZnKa lines by solving the simultaneous equations (1) for the ZnL\(_\alpha\) and ZnKa lines.

In this study the samples of the coating weight and composition in the region, \( \varnothing \), were analyzed. The following equation was used. The theoretical intensity of the ZnKa line, \( 'I_{ZnKa} \), is the same as Eq. (1).

Equation (1) becomes Eq. (4) by Taylor expansion and approximation.

\[
I_{ZnKa} = \frac{k_{ZnKa} \cdot I_{\alpha} \cdot W_{Zn}}{\sin \phi} \left[ \rho_{Fe-Zn} \cdot t \cdot \frac{1}{2} \left( \frac{\mu_{Fe}}{\sin \phi} + \frac{\mu_{Zn}}{\sin \phi} \right) \right.
\]

\[
+ \left. \left( \frac{\mu_{Fe}^{ZnKa} - \mu_{Fe}^{Zn}}{\sin \phi} + \frac{\mu_{Zn}^{ZnKa} - \mu_{Zn}^{Zn}}{\sin \phi} \right) \right) W_{Zn} \rho_{Fe-Zn} \cdot t \cdot \phi \right]
\]

where, \( k_{ZnKa} \): coefficient
\( \mu_{Fe}, \mu_{Zn} \): mass absorption coefficients of incident X-ray (\( \lambda \)) for Fe and Zn
\( \mu_{Fe}^{ZnKa}, \mu_{Zn}^{ZnKa} \): mass absorption coefficients of ZnKa line for Fe and Zn.

Equation (4) leads to Eq. (5) since the mass absorption coefficients and the incidence and takeoff angles are constant.

\[
I_{ZnKa} = a \cdot (Zn\%) \cdot x_{Fe-Zn} + b \cdot (Zn\%) \cdot x_{Fe-Zn}^2 + c \cdot (Zn\%)^2 \cdot x_{Fe-Zn} + d,
\]

\[
..................(5)
\]

where, \( x_{Fe-Zn} (= \rho_{Fe-Zn} \cdot t) \): coating weight
\( a, b, c, d \): coefficients (\( d \): background term).

The coating weights were determined by using Eq. (5).

The relationships between critical coating weight and composition in the Ni-Zn alloy coatings were calculated as shown in Fig. 4. The Ni-Zn alloy coatings were analyzed in the same procedure described above for the Fe-Zn alloy coatings.

**III. Experiments**

1. **Apparatus**

A wavelength-dispersive X-ray fluorescence spectrometer was used. Tables 3 and 4 give the specifications and the analytical conditions, respectively.

The diffraction angles \( 2\theta \) to the RAP (Rubidium...
acid Phthalate) crystal lattice spacing, \(d=26.1 \text{ Å}\), were calculated for the K and L line fluorescent X-rays of Fe, Ni and Zn elements from Bragg's equation \((2d \times \sin \theta = n \times \lambda, d: \text{crystal lattice spacing}, \theta: \text{Bragg angle}, \lambda: \text{wavelength of X-rays}, \text{and } n: \text{order of reflection})\) as shown in Fig. 5. For the measurement of the ZnLa line intensity, the interference of higher order X-ray reflection and fluorescent X-rays of the RAP crystal (RbLa, 7.3 Å) were reduced by the pulse-height selection as shown in Fig. 6.

2. Experimental Results and Discussion

Electroplated coatings of Fe–Zn alloy were analyzed. Table 5 shows the samples used for the experiments. The Fe–Zn alloy was electroplated in the plating bath from iron (II) sulfate and zinc sulfate. The substrates were a cold rolled steel sheet and a copper sheet. The Fe–Zn alloy coatings were dissolved in a hydrochloric acid solution and the Fe and Zn concentrations were determined by ICP (Inductively Coupled Plasma Spectroscopy) method. The amounts of Fe and Zn were converted to the coating weights and compositions. The high Zn % coating samples had a range of Zn % from 72.2 to 89.6 % and coating weight from 9.3 to 29.9 g/m². The coating compositions of these samples can be determined from the ZnLa line intensities as shown in Fig. 3. The ZnLa line intensities were not a function of the coating weight. The data plots for the steel and copper substrate samples had small deviations from the curve. In the acid dissolution of the Fe–Zn alloy electroplated coating steel sheet, the error in the ICP analytical values by dissolving the steel material was not significant as can be seen from Fig. 7.

The calibration curve is of a concave shape because the ZnLa line X-rays are more absorbed by Fe than by Zn. The relationship between the ZnLa line intensity and Zn % was expressed by a regression curve. The X-ray analytical value of each sample was calculated with the regression equation. The analytical accuracy \(\sigma = \sqrt{\sum (d - \bar{d})^2 / (n-1)}, \text{d: (X-ray analytical value)-(ICP analytical value); n: number of samples)}\) was 0.70 %.

| Table 3. Specifications of X-ray fluorescence spectrometer. |
|----------------------|----------------------|
| X-ray tube           | Target: Cr           |
| Rating: 2.7 kW       | R: NiKα, ZnKα       |
| Window: Be 400 μm    |                      |

<table>
<thead>
<tr>
<th>Table 4. Analytical conditions.</th>
</tr>
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<tbody>
<tr>
<td>Alloy coating</td>
</tr>
<tr>
<td>Analytical line</td>
</tr>
<tr>
<td>Operation (kV-mA)</td>
</tr>
<tr>
<td>Measuring time (s)</td>
</tr>
<tr>
<td>Crystal</td>
</tr>
<tr>
<td>Sample holder mask</td>
</tr>
</tbody>
</table>

Fig. 5. Diffraction angles of K and L line X-rays of Fe, Ni and Zn elements calculated for RAP lattice spacing. The integers in parentheses give the orders of reflection.

Fig. 6. Pulse-height distribution curve for samples of Zn, Fe and Ni.
The coating weight was determined from the ZnKα line intensity from Eq. (5). The coefficients, $a$, $b$, $c$, and $d$, were obtained by linear multiple regression analysis from the intensities, coating weights and Zn % of the samples shown in Fig. 7. In the determination of coating weights, the ZnKα line intensities and the determined Zn % were used. The analytical results of coating weights are shown in Fig. 8. The analytical accuracy was satisfactory of 0.63 g/m².

The samples of high Fe % coatings were analyzed. The substrate was a copper sheet. The samples had a range of Zn % from 5.1 to 33.6 % and coating weight from 9.8 to 11.0 g/m². The coating weights were more than the calculated critical coating weights shown in Fig. 3. Figure 9 shows the relationship between the ZnLa line intensity and Zn %. The coating weight was not determined because the coating weight of the samples was in a limited range and the determination results for the high Zn % coatings were shown above.

The Ni–Zn alloy electroplated steel sheets were analyzed. Table 6 shows the samples used for the experiments. Figure 10 shows the relationship between the ZnLa line intensity and Ni %. The samples had a range of Ni % from 0 to 20.9 % and coating weights from 12.7 to 53.8 g/m². The ZnLa line intensities were a function of Zn % for these samples. A satisfactory analytical accuracy $\sigma_d$ of 0.36 % was obtained. The coating weights were determined from the NiKα line intensities and the determined compositions as:

$$I_{NiKα} = a' \cdot (Ni%) \cdot x_{Ni-Zn} + b' \cdot (Ni%) \cdot x_{Ni-Zn}^2 + c' \cdot (Ni%)^2 \cdot x_{Ni-Zn} + d'$$

where, $I_{NiKα}$: NiKα line intensity

$x_{Ni-Zn}$: coating weight of Ni–Zn alloy coating

$a'$, $b'$, $c'$, $d'$: coefficients.

The analytical results of coating weights are shown in Fig. 11. The analytical accuracy $\sigma_d$ was 0.39 g/m².

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**Fig. 7.** Relationship between ZnLa line intensities and Zn % for Fe–Zn alloy coatings.

**Fig. 8.** Analytical results of Fe–Zn alloy coating weights.

**Fig. 9.** Relationship between ZnLa line intensities and Zn % for Fe–Zn alloy coatings.

**Fig. 10.** Relationship between ZnLa line intensities and Ni–Zn alloy coating compositions.

**Table 6.** Samples of Ni-Zn electroplated coating on steel.

<table>
<thead>
<tr>
<th>No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (%)</td>
<td>0.0</td>
<td>6.7</td>
<td>7.6</td>
<td>13.3</td>
<td>11.9</td>
<td>11.2</td>
<td>20.9</td>
<td>8.4</td>
<td>6.7</td>
<td>13.0</td>
<td>12.1</td>
<td>11.2</td>
<td>20.0</td>
<td>8.9</td>
</tr>
<tr>
<td>Coating weight (g/m²)</td>
<td>23.5</td>
<td>22.0</td>
<td>15.7</td>
<td>39.0</td>
<td>20.0</td>
<td>33.8</td>
<td>12.7</td>
<td>15.6</td>
<td>20.2</td>
<td>38.1</td>
<td>19.2</td>
<td>33.2</td>
<td>12.8</td>
<td>14.9</td>
</tr>
</tbody>
</table>
In the experiments, a Cr target X-ray tube and a RAP analyzing crystal were used for the measurement of the ZnLa line intensity. A Rh target X-ray tube and a TAP (Thallium Acid Phthalate) crystal are more excellent in sensitivity. The analytical precision is thought to be improved by using the Rh X-rays and TAP crystal. The in-depth heterogeneity of coating composition will cause large errors and the sample must be homogeneous for the X-ray fluorescence analysis, especially with the ZnLa line.

IV. Conclusion

The X-ray fluorescence analysis with the K and L series emissions was applied to the Fe–Zn and Ni–Zn alloy electroplated coatings. The composition was determined from the ZnLa line intensity for the alloy coatings in the ordinary coating weight range. The coating weight was determined from the K series line intensity (ZnKa line for Fe–Zn coating and NiKa for Ni–Zn) and the composition which was obtained above. The analytical accuracies of coating composition and weight were 0.70 % and 0.63 g/m² for the Fe–Zn alloy coating and 0.36 % and 0.39 g/m² for the Ni–Zn.

REFERENCES