

X-ray fluorescence analysis of zinc and zinc–iron alloy coated steel sheet

Takao Moriyama* and Kenji Kodama*

1. Introduction

Since it is possible to apply zinc to the surface of steel sheet in large quantities, hot-dipped zinc coated steel sheet is used for applications that require long period corrosion resistance, such as automotive bodies, prefab and metal buildings.

Zinc coated steel sheet can be roughly divided into zinc coated steel sheet (Galvanized steel sheet: GI) which is plated by immersing the steel sheet in a molten zinc bath and zinc–iron alloy coated steel sheet (Galvannealed steel sheet: GA) which diffuses the iron in the steel to coated zinc through the boundary of the zinc and steel by heating after plating treatment to make a zinc–iron alloy. GI capable of coating weight of 400 g/m² or more is widely used for applications requiring severe weather resistance, such as outdoor units of air conditioners, guardrails, construction materials, and so on. Since GA whose plating layer is zinc–iron alloy has the futures of that (1) it is easy to form into complex shapes because of harder plating than zinc alone and hardly adhering to the mold at the time of press molding, (2) it has excellent weldability because of its high melting point, (3) since the surface has dense irregularities, it is excellent in paint adhesion because of dense asperities on the surface, In addition to having anticorrosive property of GI, GA has been expanding its use mainly for automobile bodies with high demand for shape design.

Since alloying progresses as iron diffuses from the steel sheet into the plating layer, iron concentration in the portion near the steel sheet is high and in the plating surface is low. Figure 1 shows a schematic drawing of GA. The plating layer of GA can be roughly divided into three phases of Γ (Fe₃Zn₁₀), δ (FeZn₇), ζ (FeZn₁₃) in order of increasing iron concentration.

When the heating of the steel sheet in the alloying

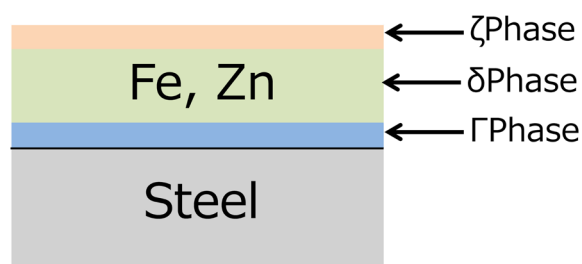


Fig. 1. Schematic diagram of layer structure of GA.

reaction is insufficient, iron concentration in the plating decreases and thickness of ζ phase on the plating surface increases. Since the ζ phase is soft and easily adheres to the metal mold, flaking phenomenon in which the plating peels off in the form of flake may occur or the steel sheet may be torn during press working⁽¹⁾.

Conversely, if iron concentration in the plating becomes too high due to overheating, Γ phase becomes thick at the interface between the plating and the steel sheet. Since the Γ phase is hard and brittle, it is said to cause a powdering phenomenon in which the compound layer is easily broken and the plating peels off in powder form at the time of press working⁽²⁾. Therefore, managing iron concentration in the plating, as well as managing the amount of zinc deposits, is indispensable for producing “high quality GA”.

In order to produce the hot-dipped zinc coated steel sheet consistently with high quality, it is important to control the coating weight of plating and is generally measured by the X-ray fluorescence spectrometry at the position where the temperature of the steel sheet has fallen to around room temperature⁽³⁾. Furthermore, in order to consistently produce high quality GA, proper control of iron concentration in the plating is also very important, and monitoring methods by on-line X-ray instruments have been developed^{(4), (5)}. In addition, batch analyses by extracting a part of a product for confirmation is important for quality control. Methods of estimating the coating weight of plating from the weight change with dissolving only the plating layer and estimating iron concentration in the plating layer by chemically analyzing the solution is widely used for batch analysis⁽⁶⁾. However, technical expertise is necessary to dissolve only the plating layer and the analysis time is too long. Also, in order to maintain high quality, it is necessary to increase the frequency of batch analysis, and therefore the number of specimens increase. For these reasons, there is a demand for a method capable of analyzing quickly and easily without any special skills. In this paper, we introduce analysis examples of hot-dip zinc and zinc–iron alloy coated steel sheets using the simultaneous wavelength dispersive X-ray fluorescence spectrometer Simultix 15 which is widely used for quality control of such products.

2. Measurement principle of hot-dip zinc and zinc–iron alloy coated steel sheet by X-ray fluorescence analysis

2.1. Measurement principle of GI

When the coating weight of plating on GI is analyzed

* SBU WDX, X-ray Instrument Division, Rigaku Corporation.

by X-ray fluorescent analysis, typically a calibration curve method using Zn-K α line as an analysis line is used⁽⁷⁾. Figure 2 shows the relationship between zinc coating weight and the Zn-K α intensity normalized by the intensity of an infinite thickness sample. With the standard optical configuration, samples with zinc coating weight up to 200 g/m² can be analyzed in practice. However, samples with higher coating weights can not be analyzed due to saturation of X-ray intensity.

This limitation is overcome on the Simultix 15 by changing the analysis line to Zn-K β_1 which has a larger analyzing depth (99% intensity of infinite thickness) than Zn-K α . In addition the take off angle was increased, and a special primary beam filter is used to increase maximum analyzable coating weight limit. Figure 3 shows the relationship between coating weight of zinc plating and intensity of Zn-K β_1 for Simultix 15 with the improvements. With the specialized optical configuration of Simultix 15, zinc coating weights up to 450 g/m² can easily be analyzed with high degree of accuracy.

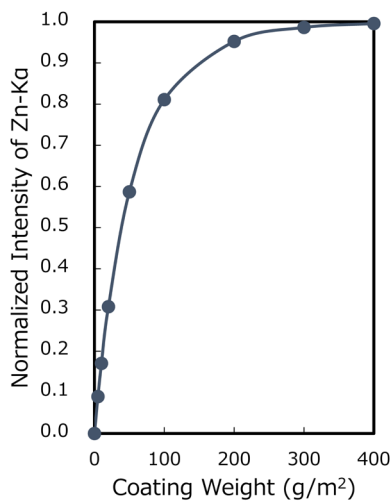


Fig. 2. Relationship between coating weight of zinc plating and the intensity of Zn-K α .

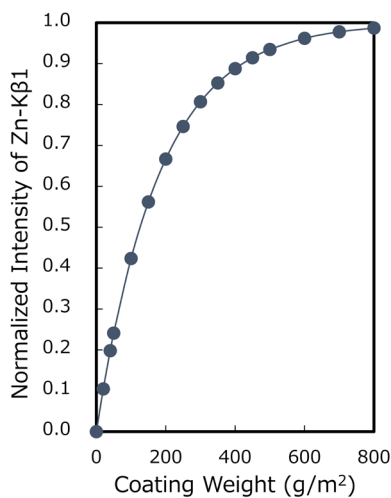


Fig. 3. Relationship between coating weight of zinc plating and the intensity of Zn-K β_1 .

2.2. Measurement principle of GA

The method described in the previous section, zinc coating weight can be measured, but not iron concentration, an important component for GA. Thin film fundamental parameter (FP) quantification method by X-ray fluorescent analysis is effective for simultaneous analysis of coating weight and composition. Thin film FP method for GA is typically performed by combining Zn-K α for the measurement of deeper sample region with Zn-L α for shallow region. However, since the analyzing depth of Zn-L α is too shallow, only the information of the surface layer, not the entire plating layer, can be obtained, and therefore accurate analysis of entire plating layer is not possible. Figure 4 compares iron concentrations in the plating layer by chemical and XRF analysis by the thin film FP method with Zn-K α and Zn-L α . The accuracy is 1.59 mass% for iron concentration range of 8 mass% to 13 mass%, which is insufficient for quality control.

Simultix 15 overcomes these problems with a specialized optical system. Accurate simultaneous analysis of coating weight and iron concentration is realized by optimizing the analysis lines and optical configuration illustrated in Fig. 5⁽⁸⁾⁻⁽¹²⁾.

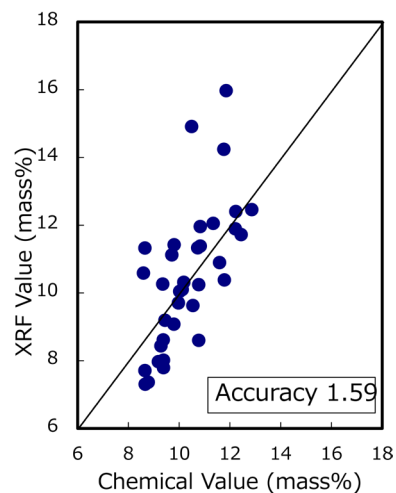


Fig. 4. Comparison of iron concentration between chemical and XRF analysis values by the thin film FP method with Zn-K α and Zn-L α .

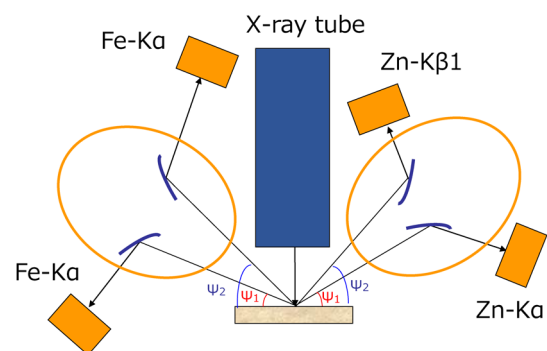


Fig. 5. Schematic diagram of special optical system for GA.

Table 1 shows analyzing depths of zinc-iron alloy layer obtained by theoretical calculation for different analysis lines and take off angles. The thin film FP method determines both iron concentration and coating weight by solving simultaneous equations from two measured intensities. The larger the difference in analyzing depth between the two analysis lines, the more accurate the analytical value of iron concentration and coating weight. It is also important that the analyzing depth of analysis lines used for the thin film FP method is larger than the thickness of the plating layer. Combinations of Zn-K β_1 (take off angle: 40 degrees) and Zn-K α (take off angle: 20 degrees) satisfy these conditions sufficiently and have been shown to be most suitable for analysis of GA.

When actually measuring the coating weight and composition by the thin film FP method using analysis lines with different take off angles, there are two potential sources of error. First, large change in the result of coating weight and composition occur by small variation in measured intensity and second, a sample height variation can influence coating weight and composition of results.

In order to reduce these errors, in Simultix 15, intensities of Zn-K α and Zn-K β_1 are divided by intensities of Fe-K α having the same take off angles respectively, and the thin film FP method uses the

Table 1. Analyzing depths of zinc-iron alloy layer for each analysis line and take off angle obtained by theoretical calculation (calculation conditions: 50 kV tube voltage, 90 degree incident angle).

Analysis line	Take off angle (degree)	Analyzing depth (g/m ²)
Zn-K α	32	227
Fe-K α	32	165
Zn-L α	32	10
Zn-K α	40	264
Zn-K β_1	40	325
Zn-K α	20	159
Fe-K α	40	190
Fe-K α	20	117

Table 2. Influence by change of sample height on X-ray intensity/X-ray intensity ratio and analysis value (a sample height is increased by 0.25 mm).

	Difference
Using X-ray intensity	
Zn-K β_1	1.60%
Zn-K α	1.90%
Coating weight (g/m ²)	0.62
Iron concentration (mass%)	-0.69
Using X-ray intensity ratio	
Zn-K β_1 /Fe-K α	0.0%
Zn-K α /Fe-K α	0.30%
Coating weight (g/m ²)	-0.25
Iron concentration (mass%)	0.11

intensity ratios of Zn-K α (take off angle: 20 degrees)/Fe-K α (take off angle: 20 degrees) and Zn-K β_1 (take off angle: 40 degrees) / Fe-K α (take off angle: 40 degrees). Table 2 shows differences of measured intensities and analyzed results between using intensity ratios and direct intensities when a sample height is increased by 0.25 mm. This table clearly shows that using the intensity ratio reduces errors due to the sample height.

3. Measurement examples of hot-dip zinc and zinc-iron alloy coated steel sheet

3.1. Measurement example of GI

Figure 6 shows the relationship of coating weight between chemical analysis values and XRF analysis values obtained by using Simultix 15. Measurement conditions are shown in Table 3. Chemical analysis values and X-ray analysis values are in good agreement, and the accuracy of coating weight is 4.57 g/m² in the range of 150 to 450 g/m².

Table 4 shows a measurement repeatability of a sample. The coefficient of variation (C.V.) of coating weight (402.2 g/m²) is 0.26%, and good measurement repeatability is obtained.

3.2. Measurement example of GA

Figure 7 shows the relationship of coating weight and

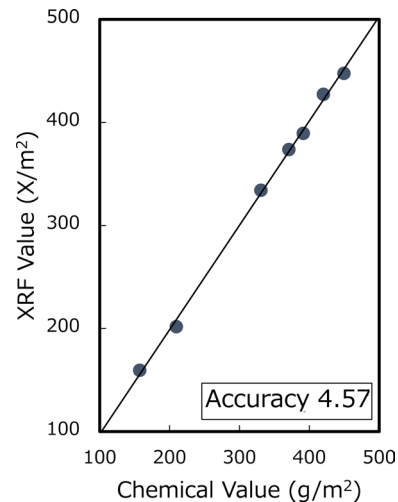


Fig. 6. Relationship of coating weight between chemical analysis value and XRF analysis value.

Table 3. Measuring conditions.

System	Simultaneous wavelength dispersive X-ray fluorescence spectrometer Simultix 15
X-ray tube	Rhodium, end window type
Tube voltage and current	50kV-50 mA
Measuring time	40 sec
Measuring diameter	30 mm
Path atmosphere	Vacuum

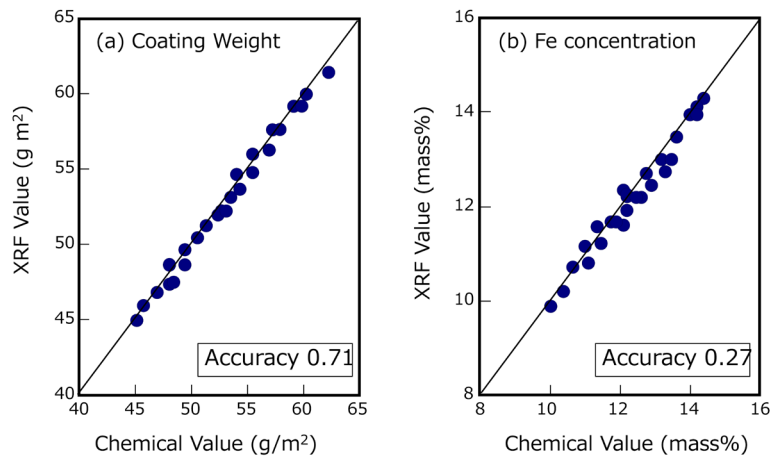


Fig. 7. Relationship of (a) coating weight and (b) iron concentration between chemical analysis value and XRF analysis value.

Table 4. Result of repeatability for the same GI sample.

Number of measurements	Coating weight g/m ²
1	400.6
2	401.8
3	401.7
4	402.3
5	402.5
6	401.8
7	402.8
8	404.5
9	401.3
10	402.5
Average	402.2
Standard deviation	1.04
C.V. (%)	0.26

Table 5. Result of repeatability for the same GA sample.

Number of measurements	Coating weight g/m ²	Iron concentration mass%
1	50.36	12.07
2	50.38	12.11
3	50.40	12.09
4	50.41	12.10
5	50.37	12.11
6	50.42	12.06
7	50.35	12.08
8	50.43	12.10
9	50.34	12.08
10	50.32	12.11
Average	50.38	12.09
Standard deviation	0.036	0.018
C.V. (%)	0.07	0.15

iron concentration between chemical analysis values and XRF analysis values obtained by using Simultix 15 with the thin film FP method. Measurement conditions are

same as previous subsection. Chemical analysis values and X-ray analysis values are in good agreement, and the accuracy of coating weight and iron concentration in plating layer are 0.71 g/m² and 0.27 mass%, respectively. Table 5 shows a measurement repeatability of a sample. The coefficient of variation (C.V.) of coating weight (50.4 g/m²) and iron concentration (12.1 mass%) are 0.07% and 0.15%, respectively, and good measurement repeatability is obtained.

4. Conclusion

Analysis examples of Simultix 15 are shown for hot-dip zinc and zinc-iron alloy coated steel sheet. In case of GI, it is possible to accurately measure thick plating of 400 g/m² or more by optimizing analysis line and take off angle. In case of GA analysis by using Simultix 15, since it is unnecessary to dissolve samples like chemical analysis and possible to simultaneously measure coating weight and iron concentration in the plating layer by using Simultix 15, it greatly shortens analysis time in batch analysis in which the number of measurement samples is expected to increase dramatically as the production volume increases.

Currently, in steel sheets for automotive body, the usage rate of steel sheet with high specific strength such as advanced high strength steel sheet is increasing in order to achieve both weight reduction for the purpose of reducing fuel consumption and securing of safety. In order to realize a high specific strength, the structure of the steel sheet is controlled by adding alloy elements such as Ni, Mn, Si and Nb⁽¹³⁾. Depending on the steel type, alloying elements added is 20 mass% or more. When such a steel sheet is galvanized, alloy elements as well as iron diffuse into the plating layer. Since certain conditions are defined for the composition of steel sheet and elements in the plating layer in FP calculation, sufficient accuracy may not be obtained if a single calibration for thin film FP calculation is applied to galvanized steel sheets with different steel plate composition. In this case, sufficient accuracy can be obtained by dividing the thin film FP calibration for each

steel type for the analysis of galvanized steel sheets.

References

- (1) M. Urai, J. Iwaya, M. Iwai and M. Arimura: *Kobe Steel Engineering Reports*, **47** (1997), 29–32.
- (2) M. Sakurai, L. W. Zhang, Y. Tajiri and T. Kondo: *Tetsu-to-Hagane*, **77** (1991), 979–986.
- (3) H. Takahashi: *Journal of The Surface Finishing Society of Japan*, **68** (2017), 610–616.
- (4) J. Kawabe, H. Hashimoto, R. Ohta and S. Takahashi: *Tetsu-to-Hagane*, **73** (1987), S1187.
- (5) K. Nishifuji, H. Tanabe, K. Imai, H. Kato and A. Honda: *Bulletin of the Japan Institute of Metals*, **30** (1991), 307–309.
- (6) ISO 1460, Metallic coatings—Hot dip galvanized coatings on ferrous materials—Gravimetric determination of the mass per unit area (1992).
- (7) JIS G 3302, Hot-dip zinc-coated steel sheet and strip (2010).
- (8) Rigaku Corporation, X-ray fluorescence spectrometer, United States Patent 7356114, 2008. 4. 8.
- (9) Rigaku Corporation, X-ray fluorescence spectrometer, Korea Patent 101046018, 2011. 7. 1.
- (10) Rigaku Corporation, X-ray fluorescence analyzer, China Patent 1932493, 2012. 1. 4.
- (11) Rigaku Corporation, X-ray fluorescence spectrometer and x-ray fluorescence measurement method, EU Patent 1764612, 2015. 4. 15.
- (12) Y. Kataoka, H. Kohno, E. Furusawa and M. Mantler: *X-Ray Spectrometry*, **36** (2007), 221–225.
- (13) M. Takahashi: *Tetsu-to-Hagane*, **100** (2014), 82–93.