Journal of Surface Analysis Vol.20, No. 3 (2014) pp. 202−206
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Paper

Comparative Study on Nondestructive and Destructive Methods of Evaluating Thicknesses of Hot-dip Galvanized Coatings

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(Received : November 12, 2013; Accepted : January 24, 2014)

Two on-site nondestructive methods, one involving an electromagnetic thickness tester and the other a handheld x-ray fluorescence analysis system, were used to evaluate thicknesses of hot-dip galvanized coatings on steel and compared with destructive analytical methods. They were sufficiently applicable for measuring the remaining thickness or mass of the coatings when the density of the alloy layer or the zinc depth profile was already known.

1. Introduction

Hot-dip zinc-coated steel is one of the main structural materials for outdoor plants including telecommunication equipment (steel poles, towers, strand wires, etc.) because of the sacrificial protection effect of zinc on steel against atmospheric corrosion [1]. The International Organization for Standardization (ISO) provides the standards for hot-dip zinc-coated steel products (e.g. ISO 3575, 4998) and coatings (ISO 1461). The Japan Industrial Standard (JIS) provides almost the equivalent or modified standards of sheets, coils, wires, wire strands (JIS G 3302, 3548, 3537) and coatings (JIS H 8641), where the minimal thicknesses are specified and classified basically by the mass of zinc deposit per unit area (called simply "mass", hereafter), except for classes HDZ A and B. For example, the mass should be more than 550 g/m2 for the class HDZ 55. Direct and indirect methods for evaluating the mass are provided in JIS H 0401, where direct and indirect mean in-process (by measuring weight gain after galvanizing) and after-process (by testing galvanized products).

The remaining galvanized coating thickness of the equipment is the important for effective protection against corrosion and guaranteeing adequate reliability. To evaluate thickness, nondestructive and on-site indirect test methods are suitable from the viewpoint of usefulness and convenience in inspection. We chose two nondestructive methods among those concerning the thickness of metallic coatings provided in JIS H 8501 corresponding to ISO 3497: the electromagnetic method and x-ray fluorescence analysis (XRF) for galvanized coating on steel. The electromagnetic method involving an electromagnetic thickness tester (EM tester) is also mentioned in JIS H 0401, where 7.2 g/cm^3 is used as the density of galvanized coating to convert thickness to mass. The EM tester is a popular testing tool due to its simplicity and portability. The XRF, which is a rather analytical method, is generally used for quality control of coating thickness in plating or galvanizing processes and is often embedded in a factory automation system. However, several handheld XRF systems have recently been developed that are portable and usable either indoor or outdoor if statutory and safety requirements are satisfied, *e.g.*, on-site discrimination of valuable metals for recycling and on-site screening of hazardous substances for soil pollution [2].

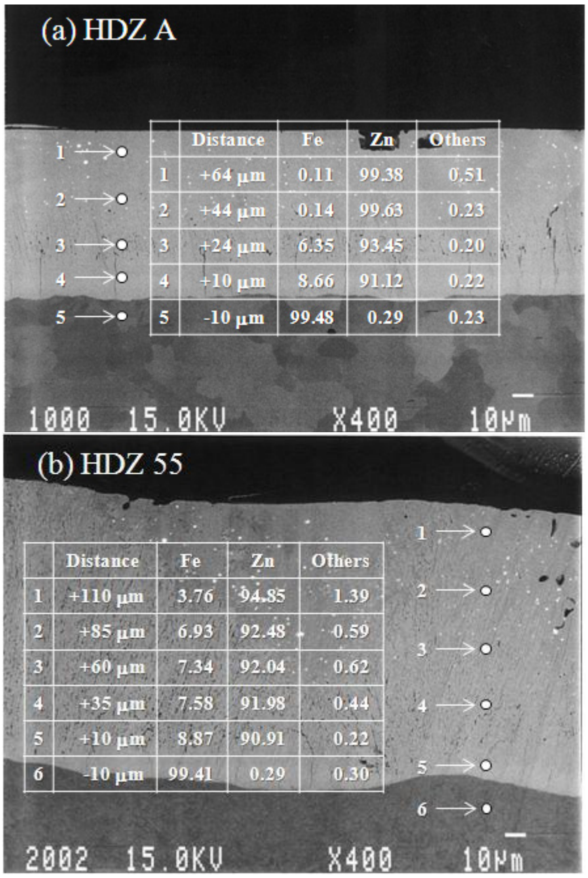
We prepared sample series with different zinc coating thicknesses and used an EM tester and a handheld XRF system. We discuss their applicability in evaluating hot-dip galvanized coatings on steel by comparing them with destructive methods: cross-sectional observation, chemical dissolution method, and glow-discharge optical emission spectroscopy (GD-OES).

2. Experimental

Two types of hot-dip zinc-coated SS400 steel sheet samples, HDZ A and HDZ 55, were prepared. The former is generally used for thinly coating small and/or thin steel parts. The latter is for steel products used in corrosive environment such as coastal areas where metallic equipment is subjected to heavy sea-salt damage. The coating thickness of HDZ A should be at least 28-42 μm and that of HDZ 55 should be more than 76 μm according to JIS H 8641. We prepared the HDZ 55 sample series by cutting a sheet into pieces, dipping some of the pieces in dilute hydrochloric acid to etch their coatings, and controlling the remaining thicknesses by adjusting the etching time. We used a chemical dissolution method according to JIS H 0401 to measure their mass. The samples were dipped in hydrochloric acid with hexamethylenetetramine and their weight losses were measured. An optical microscope was used to observe cross-sections of the original coatings after the cross-sectional samples were mechanically and chemically polished (not processed by additional chemical etching). A scanning electron microscope (SEM) - electron-probe microanalyzer (EPMA) system (JEOL JXA-8621) was used for semi-quantitative analysis of the internal composition in the coatings. The accelerating voltage was 15 kV. The GD-OES measurements were conducted using the Horiba GD Profiler 2 operated in a constant power mode (35 W). The argon gas pressure was 600 Pa, and the diameter of the sputter crater was 4 mm. We used the SWT-8000 II system (Sanko Electronic Laboratory) as a general EM tester. The distance between the sensor head and the underlying ferromagnetic surface, which should correspond to the thickness of the non-magnetic coating on steel, is detected as the change in inductance of the inner electromagnetic coil embedded at the back of the sensor head. After calibration including zero adjustment, the thickness of the non-magnetic coating was measured. The electromagnetic method is described as a method for measuring the coating thickness of electrolytic and chemical plating in JIS H 8501 corresponding to ISO 2178 as well as cross-sectional optical microscope observation. We used a handheld XRF system, Horiba MESA 330 Portable, to measure x-ray fluorescence intensities from the samples. The rhodium x-ray tube was operated at 45 kV and 40 μA. This XRF method is also described in JIS H 8501. We chose the excitation method using zinc x-ray intensities among the two methods described in JIS H 8501.

3. Results and discussion

As the results of cross-sectional optical microscope observation, the mean thicknesses of the original coatings were about 66 μm for HDZ A and about 114 μm for HDZ 55. Some layers having different contrasts were observed in the HDZ A coating, while not clearly observed in the HDZ 55 coating. Figure 1 show the cross-sectional SEM images of the original coatings including EPMA semi-quantification result tables. Figure 2 shows in-depth compositional profiles of the coatings of (a) HDZ A and (b) HDZ 55 measured using GD-OES. The EPMA results in Fig. 1 (a) show the existence of the almost pure zinc layer around points 1 and 2 in the HDZ A coating, which also corresponds with the zinc depth profile of Fig. 2(a). This layer is thought to be the η phase. It is known that zinc-iron binary alloy systems can take various phases with different compositional ratios (η, ζ, δ_1, Γ_1, Γ, etc.) and the phase formation is affected



	Distance	Fe	Zn	Others
1	+64 μm	0.11	99.38	0.51
2	+44 μm	0.14	99.63	0.23
3	+24 μm	6.35	93.45	0.20
4	+10 μm	8.66	91.12	0.22
5	-10 μm	99.48	0.29	0.23

	Distance	Fe	Zn	Others
1	+110 μm	3.76	94.85	1.39
2	+85 μm	6.93	92.48	0.59
3	+60 μm	7.34	92.04	0.62
4	+35 μm	7.58	91.98	0.44
5	+10 μm	8.87	90.91	0.22
6	-10 μm	99.41	0.29	0.30

Fig. 1 Cross-sectional SEM images of original (a) HDZ A and (b) HDZ 55 coatings including EPMA semi-quantification result tables (% in weight). Open circles indicate points analyzed using EPMA. Approximate distances from interfaces are also shown in tables.

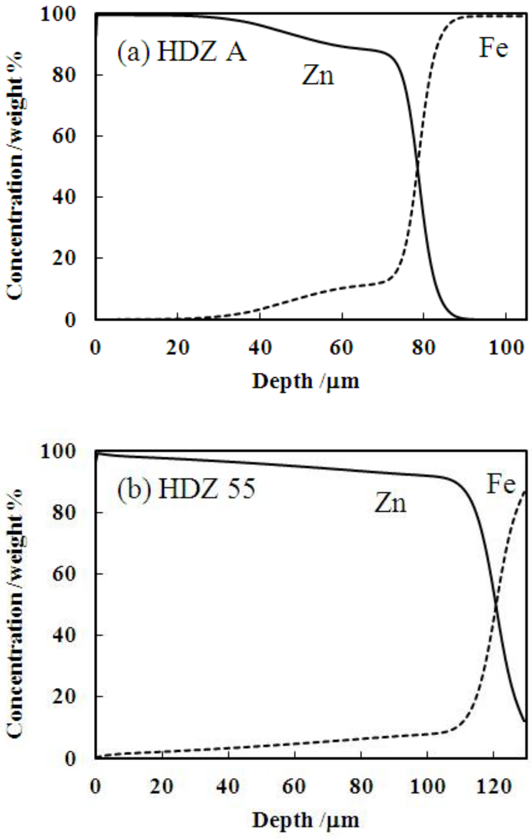


Fig. 2 Depth profiles of zinc and iron measured using GD-OES.

by galvanizing conditions and co-existing trace elements [3]. In Fig. 1 (a), the region around point 3 where the iron concentration is 6.35% is thought to be the ζ phase of the HDZ A coating. This phase, in which the iron concentration widely ranged around 6%, might be thickly formed in the HDZ 55 coating by assumption from the zinc and iron depth profiles of Fig. 2 (b). In Fig. 2 (a), the composition plateau at 50-60 µm near the interface seemed to be the δ_1 phase of the HDZ A coating. The HDZ 55 coating might also have the δ_1 phase layer but it might be thinner. We may also determine the coating thicknesses by using the cross points of the zinc and iron profile at 50% by assuming a constant sputter rate, certain depth resolution, and unchanged sensitivity factors during measurement: 78 µm for HDZ A and 121 µm for HDZ 55.

With the chemical dissolution method, the masses of zinc of the original and etched samples were given and the coating thicknesses were calculated on the assumption that the coatings consisted of pure zinc with a density (ρ) of 7.14 g/cm^3. Figure 3 shows the relationship between the thicknesses of the HDZ 55 samples measured using the EM tester and evaluated using the chemical dissolution method. The solid line is the line obtained using the least-squares method. The slope (β) and intercept (α) at the coordinate were 1.05 and 8.01 µm, respectively. Assuming the simple model of HDZ 55 shown in Fig. 4, we can describe the relationship between the thicknesses obtained using the EM tester (d_m) and chemical dissolution method (d_c),

$$c_r\rho_r d_r + c_n\rho_n d_n + c_f\rho_f d_f = \rho d_c \qquad (1)$$

and rewrite Eq. (1) as

$$d_m = \frac{\rho}{c_n\rho_n} d_c + \left(1 - \frac{c_r\rho_r}{c_n\rho_n}\right) d_r - \frac{c_f\rho_f}{c_n\rho_n} d_f \qquad (2)$$

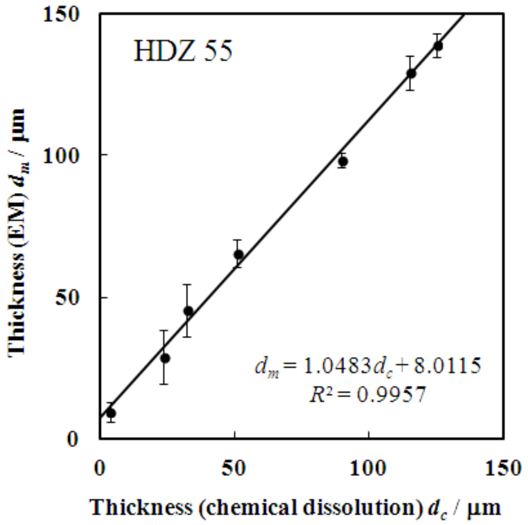


Fig. 3 Relationship between thicknesses measured using EM and chemical dissolution methods.

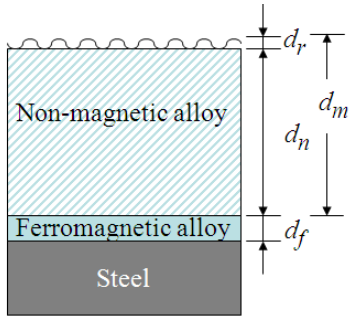


Fig. 4 Simple model of HDZ 55 coating having three layers with different thicknesses.

where $d_m = d_r + d_n$, the concentrations c denote the mean weight concentrations of zinc, and subscripts r, n, and f denote the roughness layer, non-magnetic alloy layer, and ferromagnetic alloy layer, respectively (where non-magnetic means “not ferromagnetic” and includes paramagnetic and diamagnetic). The d_m value should be thicker than d_c basically by a factor of β, which is given as ρ over $c_n\rho_n$ in Eq. (2). Using β obtained in Fig. 3, c_n was then calculated to be 0.95, which was reasonable in comparison with the expected mean zinc concentration in the HDZ 55 coating in Fig. 2(b). The ρ_n value was also calculated to be 7.17 g/cm^3, which corresponded well to 7.2 g/cm^3 described in the reference of JIS H 0401. Thus, d_m can be calculated from d_c by using Eq. (2) under the assumption of non-magnetic alloy density, and vice versa. This shows the applicability of the EM tester for HDZ 55, except for the small gap shown as α, which is expressed as the sum of the second and third terms on the right side of Eq. (2). The roughness layer may apparently include half air and half zinc in volume (iron is ignored) and $c_r\rho_r$ can then be given as a half value of ρ, 3.57 g/cm^3 The ferromagnetic layer at the interface was supposed to include half zinc and half iron in weight (c_f and ρ_f can then be 0.5 and 7.49 g/cm^3). Therefore, Eq. (2) is expressed as

$$d_m = 1.05 d_c + 0.48 d_r - 0.55 d_f. \qquad (3)$$

This equation indicates that d_r acts as a factor in increasing α in Fig. 3, resulting in over-estimation of the zinc amount. To the contrary, the thickness of the ferromagnetic layer d_f results in under-estimation. In this HDZ 55 series, d_r was larger than d_f since α was positive.

Figure 5 shows the x-ray fluorescence intensities of zinc (ZnKα) and iron (FeKα) measured using MESA 330 versus the thicknesses obtained using the chemical dissolution method. Assuming that an element is homogeneously included in a coating (concentration c) and not in underlying layers and its characteristic fluorescent x-ray is produced only by the excitation at the single wavelength of the incident x-ray, the dependence of the x-ray fluorescence intensity I on coating thickness d is theoretically expressed as

$$I \propto \frac{c}{A}\left(1-\exp\left(-Ad\right)\right) \qquad (4)$$

where

$$A = \frac{\mu\left(\lambda_i\right)}{\sin\theta} + \frac{\mu\left(\lambda_f\right)}{\sin\phi} \qquad (5)$$

Here, $\mu(\lambda_i)$ and $\mu(\lambda_f)$ express the absorption coefficients at the wavelengths λ_i and λ_f of incident and fluorescent x-rays, and θ and ϕ are the incident and detecting angles to the sample normal, respectively. For the Zn-Fe binary alloy having in-depth compositional change, c of zinc, μ, and A are expressed as the functions of depth z, and the zinc x-ray fluorescence intensity is expressed as

$$I \propto \int_0^d c(z)\exp\left(-\int_z^d A(z)dz\right)dz. \qquad (6)$$

In Fig. 5, the measured ZnKα curve shows a small thickness offset (in the abscissa) that might have originated from the difference in the measured position of the coating. The solid line is a calculated curve from the zinc depth profile in Fig. 2 (b). If zinc profile $c(z)$ is known beforehand, the dependence of ZnKα intensity on thickness can be reconstructed, as in Fig. 5, that is, the mass of zinc can be evaluated using the handheld XRF system within the thickness range where the x-ray fluorescence intensity is not saturated.

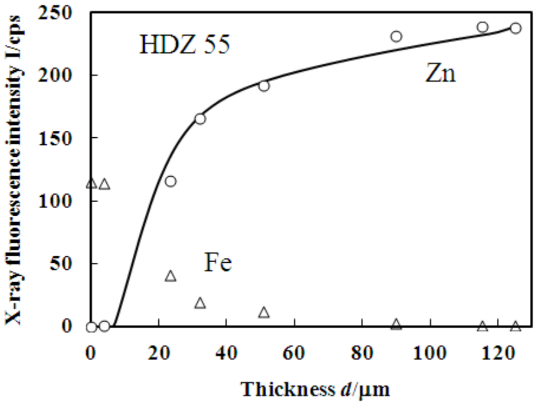


Fig. 5 Dependencies of x-ray fluorescence intensities on coating thickness (circle: Zn, triangle: Fe). Solid line is curve calculated from zinc depth profile measured using GD-OES.

4. Conclusions

We used two on-site nondestructive methods involving an EM tester and a handheld XRF system, respectively, to evaluate hot-dip galvanized coatings on steel and compared them with destructive analytical methods. Both methods were sufficiently applicable for measuring the remaining thickness or mass of the coatings when the density of the alloy layer or the in-depth compositional profile was already known. Other than the evaluation of galvanizing and/or plating metal thicknesses, the handheld XRF system, which can also be used to analyze corrosion products and environmental salt concentration [4], has a high potential as an on-site diagnosis tool for outdoor plants.

5. References

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