Control of Thickness of Corrosion-Resistant Zn-Fe, Zn-Co & Zn-Ni Coatings

By G. Bikulčius

Two methods were used to measure the thickness of zinc alloys. The results were obtained by means of coulometric and magnetic methods. They were compared with the results obtained by profilography; correction factors were found that made it possible to determine a geometrical coating thickness.

Currently, widespread use is made of zinc alloys—zinc-iron, zinc-cobalt, and zinc-nickel. Thickness measurement of these alloys has presented a problem.[1,2] In Ref. 3, a table shows applicability of different coating thickness measurement methods. Coatings of zinc on steel, for example, can be measured by beta back-scatter, coulometric and magnetic methods.

Coating thickness is usually checked by two methods: Destructive and non-destructive.[4] In addition to use of the profilograph, this study describes coulometric and magnetic methods for cases in which destructive methods are not suitable.

Experimental Procedure

Samples made of ST3 steel, 70 x 40 x 1 mm, were investigated. The surface roughness parameter, R_a, was measured by profilometer. The R_a of all samples was 0.15 µm. The samples were divided into four groups, with each group plated by an appropriate zinc alloy (Table 1). Concentrations of other metals were determined by X-ray microanalyzer.

Local Zn-Fe, Zn-Co and Zn-Ni coating thicknesses were measured in certain places on the samples (see figure). Thicknesses were determined by:

1. Use of a magnetic thickness gauge, employing the principle of magnetic induction. The measuring range was 2000 µm with accuracy of 10 percent, similar to that described in Refs. 5 and 6.
2. An electrochemical film thickness gauge, measuring metallic single- or multi-layer coatings on a metallic base by electrochemical removal of metal. It is particularly suitable for galvanic coatings. There are two measuring ranges: 0.5-3.0 µm at a rate of 0.01 µm/sec, and 3-50 µm at a rate of 0.1 µm/sec. The measuring area is one mm², with tolerance of 7 percent. It is similar to that described in Ref. 7.
3. Profilometer/profilograph. The accuracy of this method is generally better than 2 percent. Its principle is explained in Refs. 8 and 9.

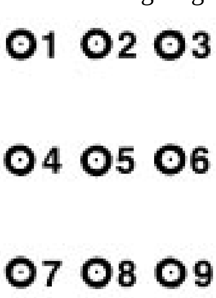

Diagram of sample measurements. Numbers 1-9 designate points of coating thickness measurements.

Local coating thicknesses ranged from 1.0 to 13.0 µm in all cases.

Correction factors were calculated by these formulas:

$$\frac{\sum_{i=1}^{n} \bar{H}_{pi} / \bar{H}_{ki}}{n} = K \quad \text{and} \quad \frac{\sum_{i=1}^{n} \bar{H}_{pi} / \bar{H}_{mi}}{n} = K$$

where $\bar{H}_p$ is the arithmetic mean of the coating thickness measured by a profilograph; $\bar{H}_k$ is the arithmetic mean of the coating thickness measured by a coulometric thickness gauge; $\bar{H}_m$ is the arithmetic mean of the coating thickness measured by a magnetic thickness gauge.

Results and Discussion

Coulometric Measurements

As can be seen from the results of measurements of zinc-iron coating thickness listed in Table 2, the data on the coating thickness when using the coulometric thickness gauge and a profilograph are very close. The percentage error does not exceed 5.0 percent. The correction factor of the coulometric method is 0.98 (Table 3).

For zinc with a considerable amount of cobalt, the error is as much as 13.0 percent in some cases. Upon calculating the correction factor, we determine that it is 0.93 (Table 3). At the same time, zinc with a small amount of cobalt shows an error of 18.0 percent. After calculating the correction factor, we find that it is 0.88 (Table 3). It would seem that with decrease in the cobalt concentration, the percentage error must also decrease. As can be seen from Table 2, however, it is not so.

Table 1
Types of Electrodeposited Zinc Alloy

Coating System	Electrolyte Comp., g/L		Operating Conditions
Zn-(0.4-0.6 at.%)Fe	ZnO	8-12	18-30 °C
	NaOH	90-100	Current density, 1-4 A/dm²
	+ Brighteners		
	+ Fe additive		
Zn-(0.8-1.0 at.%)Co	ZnO	8-12	18-30 °C
	NaOH	90-100	Current density, 1-4 A/dm²
	+ Brighteners		
	+ Co additive		
Zn-(0.38 at.%) Co	$ZnSO_4$	120	22 °C, pH5.5
	$CoSO_4$	37	2 A/dm² with
	NH_4Cl	30	air agitation
	H_3BO_3	20	
	+ Brighteners		
Zn-(18-20 at.%)Ni	NH_4Cl	200	27-35 °C
	$ZnCl_2$	50	pH 5.0
	$NiCl_2 \cdot 6H_2O$	150	4 A/dm²
	H_3BO_3	20	with air agitation
	+ Brighteners		

Table 2
Results of Thickness Measurements

Coating	H_p µm	H_k µm	α_k µm	ε_k %
Zn-(0.4-0.6 at.%)Fe	2.2	2.3	0.1	4.5
	3.6	3.7	0.1	3.0
	4.8	4.9	0.1	2.0
	10.1	10.3	0.2	2.0
Zn-(0.8-1.0 at.%)Co	2.0	2.1	0.1	5.0
	3.9	4.4	0.5	13.0
	6.3	7.0	0.7	11.0
	11.0	11.3	0.3	2.7
Zn-(0.38 at.%) Co	3.0	3.3	0.3	10.0
	6.5	7.4	0.9	14.0
	8.9	0.5	1.6	18.0
	12.3	13.3	1.0	8.0
Zn-(18-20 at.%)Ni	2.8	4.0	1.2	42.8
	5.0	6.6	1.6	32.0
	7.2	9.1	1.9	26.4
	10.3	14.0	3.7	36.0

By means of X-ray phase analysis, it was estimated that at the low cobalt concentration (4.0 atomic percent), a solid solution with zinc was formed, but when the concentration of cobalt increased to 0.8-1.0 at. pct., cobalt was present in the zinc as an independent phase.[10] In the case when the Zn-Co coating consisted of a solid solution, anodical dissolution was inhibited and the values of coating thickness measurement increased. In another case, the influence of cobalt in the coating on the results of measurement was negligible. The data on Zn-Ni coating thickness are considerably overrated. The error is as much as 43.0 percent. The correction factor is calculated to be 0.74 (Table 3). The inhibited anodic dissolution of Zn-Ni coatings can be explained by the presence of a solid Ni-Zn solution, as in the case of Zn-Co at low Co concentration, and as discussed by Shibuya *et al.*[11]

Magnetic Measurements

As can be seen from the results of measurements of Zn-Fe coating thickness, listed in Table 4, the data on coating thickness obtained when using a magnetic thickness gauge and a profilograph differ a great deal. The error is as large as 64.0 percent. Calculation of the correction factor yields 0.68 (Table 3). The thickness measurements of zinc coating with high cobalt obtained with a magnetic thickness gauge are overrated. The error is as great as 70.0 percent. Similar results for low-cobalt Zn-Co and for Zn-Ni can be seen in Table 4.

The correction factors become similar when the zinc alloy thickness is measured by the magnetic method. It should be noted that alloys not only have different concentrations of admixtures, but also the same admixtures have different magnetic properties, some of which are determined by the presence of cobalt or nickel.

Findings

This short series of experiments performed on zinc alloys has demonstrated that coulometric and magnetic gauges can be used for thickness measurement of zinc coatings and adapted to zinc alloy (Zn-Fe, Zn-Co and Zn-Ni) thickness measurement, but only for a fixed technological process.

Editor's note: *Manuscript received, September 1994; approval received, May 1997.*

Table 3
Correction Factors for Zinc Alloy Coating Thickness Measurement Methods

Coating	Correction Factor K: Coulometric Method	Correction Factor K: Magnetic Method
Zn-(0.4-0.6 at.%)Fe	0.98	0.68
Zn-(0.8-1.0 at.%)Co	0.93	0.66
Zn-(0.38 at.%) Co	0.88	0.76
Zn-(18-20 at.%)Ni	0.74	0.68

Table 4
Results of Thickness Measurements

Coating	H_p µm	H_k µm	α_k µm	ε_k %
Zn-(0.4-0.6 at.%)Fe	2.2	3.6	1.4	64.0
	3.6	5.4	1.8	50.0
	4.8	6.9	2.1	44.0
	10.1	13.4	3.3	33.0
Zn-(0.8-1.0 at.%)Co	2.0	3.4	1.4	70.0
	3.9	6.3	2.4	62.0
	6.3	9.1	2.8	44.0
	11.0	15.0	4.0	36.3
Zn-(0.38 at.%) Co	3.0	4.0	1.0	33.0
	6.5	8.6	2.1	32.0
	8.9	11.7	2.8	31.0
	12.3	15.7	3.4	28.0
Zn-(18-20 at.%)Ni	2.8	4.2	1.4	50.0
	5.0	8.2	3.2	64.0
	7.2	9.8	2.6	36.0
	10.3	14.0	3.7	36.0

References

1. M.R. Kalantary, *Plat. and Surf. Fin.*, **81**, 80 (June 1994).
2. A. Meyer, *Galvanotechnik*, No. 7, 2293 (1993).
3. ISO 3882-76.
4. GOST 9.302-88 (Russian standard)
5. ISO 2178-82.
6. Non-Destructive Coating Thickness Testers, *Metal Finishing Plant and Processes*, 120 (July/Aug. 1983).
7. ISO 2177-85.
8. ISO 4518-80.
9. Thickness Testers, *Metal Fin.*, **92**, 23 (July 1994).
10. H. Leidheiser, A. Vertus and M.L. Varsanyi, *J. Electrochem. Soc.*, **128**(7), 1456 (1981).
11. A. Shibuya, T. Kurimoto, Y. Hoboh and N. Ysuki, *Trans. Iron and Steel Inst.*, Japan, No. 11, 923 (1983).

About the Author

Dr. Gedvydas Bikulčius is a researcher at the Institute of Chemistry, A. Gostauto 9, 2600 Vilnius, MTP-1, Lithuania, where he investigates the problems of coatings. His area of interest includes physical/mechanical properties of metallic and non-metallic thin-film coatings. His interest in thickness measurement of galvanic coatings now extends beyond ten years. He is active in the Technical Committee for Standardization of Coatings, TC 7, as chairman of the subcommittee on Physical-Mechanical and Corrosion Tests.