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용융아연도금에서 비스머스 첨가에 의한 아연 수율향상에 관한 연구

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Effect of Bismuth Addition on the Zinc Consumption in Hot-Dip Galvanizing

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Abstract

Hot-dip galvanizing process is used widely in industry to achieve corrosion resistant coatings. Poor drainage during this process often leads to problems such as icicle formation and bridging. In this work, mild steel specimens were hot-dip galvanized. Influence of the addition of bismuth, aluminum and both (bismuth and aluminum) to the zinc bath on the zinc drainage were determined. Bismuth additions improved the drainage significantly. Zinc bath containing 0.1 wt.% Bi and 0.025~0.05 wt.% Al showed uniformity of coatings. Industrial trials with this bath composition showed reduction in zinc consumption, reduction of ash and dross, and good luster of workpiece.

Keywords : *Hot-dip galvanizing, Bismuth, Drainage, Zinc consumption*

1. INTRODUCTION

Hot-dip galvanizing is widely used in industry due to its process flexibility and cost effectiveness[1-3]. Drainage of excess zinc after galvanizing is controlled by the temperature, the withdrawal speed and the orientation of the workpiece. Poor drainage can lead to zinc accumulation in corners and angles on the workpiece to form icicle. It also bridges over small holes and thin channels. Therefore, extra cleaning of the workpiece may be required if these problems are severe.

Gagne[3] reported that bismuth additions improved the drainage of zinc from the galvanized workpiece and reduced dross formation. Others claimed that drainage improvement offered by the addition of bismuth to zinc bath was inconclusive. Pedersen[4] reported that drainage effects due to bismuth was minimal for the small

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flat samples used in his experiments. In this work, influence of the addition of bismuth, aluminum and both (bismuth and aluminum) on the zinc drainage were determined.

2. EXPERIMENTAL

Mild steel was used as the specimen. The specimen size was 60㎜ width, 80㎜ length and 3㎜ thick. Specimens were cleaned by HCl solution (15~20 vol.%) to remove rust on the surface. After acid cleaning, specimens were rinsed. Then the specimens were dipped in aqueous solution containing NH_4Cl and $ZnCl_2$ at temperature of 80℃ and dried in air. Two kilograms of zinc was melted and maintained at 445~455℃ in a carbon crucible. Bismuth and aluminum were added to molten zinc as mother alloys. Specimens were dipped in the zinc bath for three minutes, withdrawn and water-cooled. Each experiment was repeated five to six times to ensure reproducibility of data.

After galvanizing, the samples were dipped in copper sulfate solution to determine the uniformity of the coated layer. The tests were performed according to KS M 1610 Standard. One hundred and eighty grams of $CuSO_4$ was dissolved in 500㎖ distilled water by heating.

$Cu(OH)_2$ was added (10g per 10ℓ) to neutralize liberated H_2SO_4. The solution was prepared by filtering after 24 hours. Galvanized specimen was dipped in this solution for one minute. After pulling out, the specimen was dipped into water and copper deposited on the surface of specimen was removed by brush. This procedure was repeated until the zinc coating was removed completely.

3. RESULTS AND DISCUSSION

Figure 1 shows the effect of bismuth content in the bath on the weight gain of zinc per unit area of dipped specimen. The weight gain of zinc decreased with increase in bismuth content and became levelled off beyond 0.1 wt.%. Decrease of the weight gain means better zinc drainage from the specimen. Thus, bismuth additions improved the drainage of zinc. Very small icicles formed at the bottom corner of the specimen. Icicle formation is elaborated in later part of the discussion.

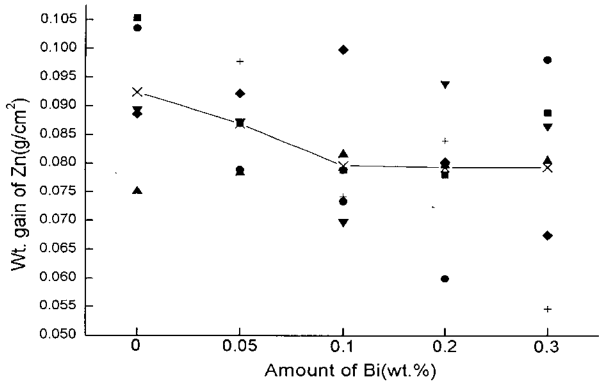


Fig. 1. Effect of Bi amount in the bath on the weight gain of Zn per unit area of specimen.

In industrial practice, small amounts of aluminum is sometimes added to zinc molten bath. So it is worthwhile to investigate the effect of aluminum addition in presence of bismuth. Figure 2 shows the weight gain of zinc as a function of aluminum content of the bath (0.025 wt.% to 0.1 wt.%) at fixed bismuth content of 0.1 wt.%. The zinc weight gain was minimum at 0.05 wt.% aluminum which was about the same value as obtained at 0.1 wt.% bismuth shown in Figure 1. Zinc weight gain when aluminum content was varied from 0.025 wt.% to 0.1 wt.%

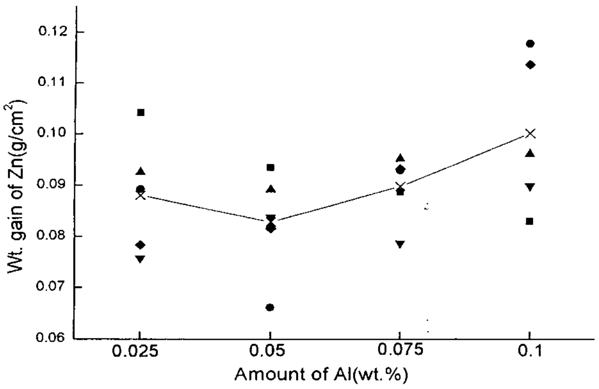


Fig. 2. Effect of Al amount in the bath on the weight gain of Zn per unit area of specimen with 0.1 wt.% Bi addition.

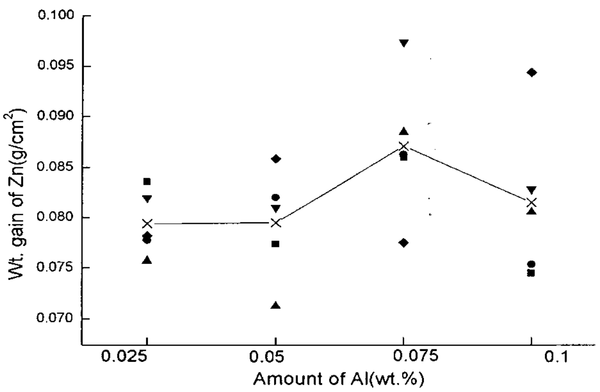


Fig. 3. Effect of Al amount in the bath on the weight gain of Zn per unit area of specimen without Bi addition.

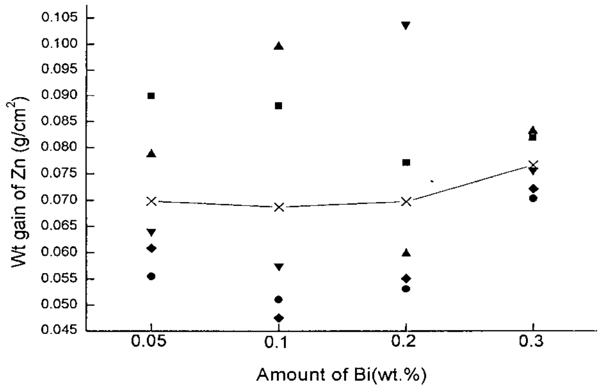


Fig. 4. Effect of Bi amount in the bath on the weight gain of Zn per unit area of specimen with 0.05 wt.% Al addition.

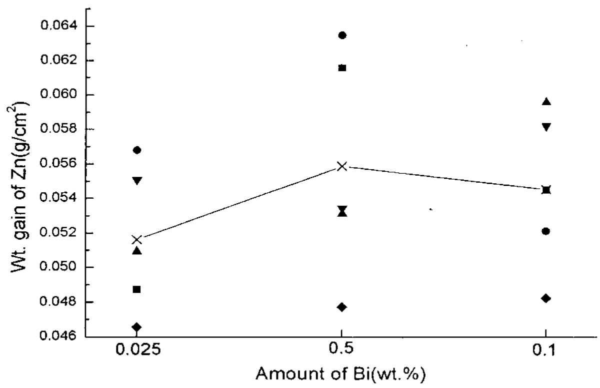


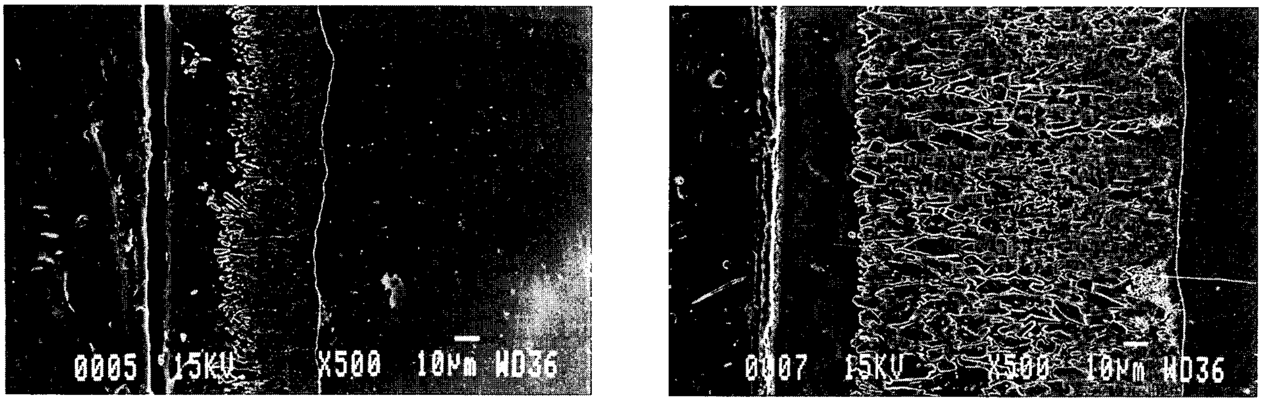
Fig. 5. Effect of Bi amount in the bath on the weight gain of Zn per unit area of specimen with 0.025 wt.% Al addition.

without bismuth addition is shown in Figure 3. Zinc weight gain was large at 0.075 wt.% aluminum.

Further experiments were performed with bath varying bismuth content from 0.05 wt.% to 0.3 wt.% and aluminum content fixed at 0.05 wt.%. The result is shown in Figure 4. Weight gain of zinc increased at 0.3 wt.% bismuth.

The result obtained when varying bismuth amount from 0.025 wt.% to 0.1 wt.% and aluminum amount fixed at 0.025 wt.% is shown in Figure 5. Zinc weight gain was very small.

Fig. 6 shows SEM micrographs of a cross section of the galvanized layers obtained with and without bismuth addition. The thickness of iron-zinc compound layer was reduced significantly by addition of bismuth. EPMA line profiles of zinc, aluminum and iron on these layers are shown in Fig. 7. Aluminum migrated to the surface of galvanized layer by adding bismuth (Fig. 7 d). Extended iron content was observed due to the thick iron-zinc compound layer formed when bismuth was not added (Fig. 7 f). About one to two grams of dross formed in all cases described above. Of all experiments performed, the amount of dross was minimum when bismuth amount was varied with aluminu-



(a) (b)

Fig. 6. SEM micrographs of a cross section of galvanized layers (a: Bi 0.1 wt.%, Al 0.025 wt.%, b: Bi 0.0 wt.%, Al 0.025 wt. %).

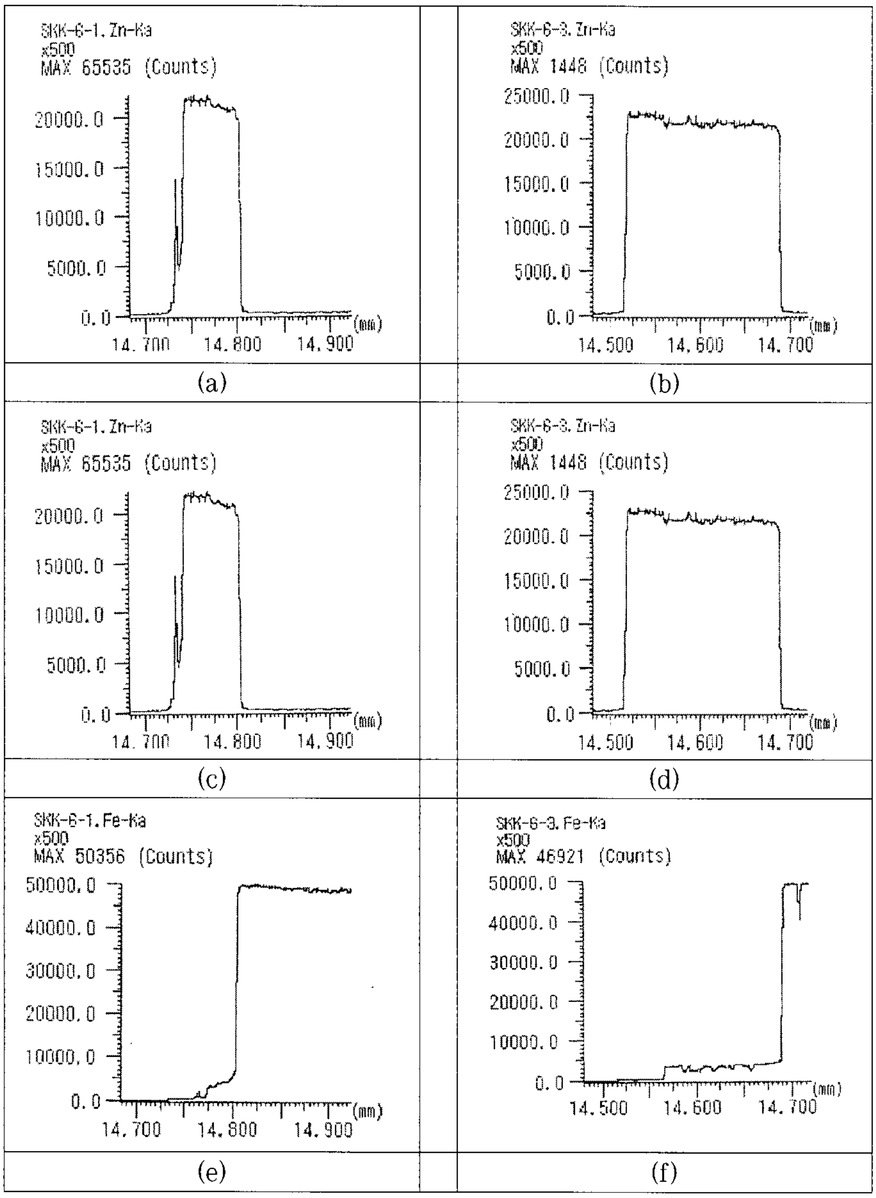


Fig. 7. EPMA line profile of galvanized layers as in Fig. 6 (a and b: Zn, c and d: Al, e and f: Fe, a, c, and e are Bi addition and b, d and f are without Bi addition).

Table 1. Frequency of zinc icicle formation

	bismuth added	aluminum added bismuth fixed	aluminum added	bismuth added aluminum fixed
Total number of Specimen	24	20	20	20
No. of specimen with icicle formed	9	13	14	10

Table 2. Number of dipping tests for removal of zinc coating (partial removal/complete removal)

Bi 0%	Bi 0.05%	Bi 0.1%	Bi 0.2%	Bi 0.3%
2/12	1/3	1/3	1/4	1/2

Bi 0.1% Al 0.025%	Bi 0.1% Al 0.05%	Bi 0.1% Al 0.075%	Bi 0.1% Al 0.1%
4/6	4/5	3/4	3/5
Al 0.025%	Al 0.05%	Al 0.075%	Al 0.1%
2/6	2/5	2/3	2/3
Al 0.05% Bi 0.05%	Al 0.05% Bi 0.1%	Al 0.05% Bi 0.2%	Al 0.05% Bi 0.3%
3/5	3/5	2/3	2/3

Al 0.025% Bi 0.025%	Al 0.025% Bi 0.05%	Al 0.025% Bi 0.1%
3/6	3/4	3/5

m amount fixed at 0.05 wt.% and 0.025 wt.%. Frequency of zinc icicle formation is summarized in Table 1. It can be inferred from Table 1 that varying bismuth content of the bath with and without aluminum reduced the frequency of zinc icicle formation.

Brightest coating luster was obtained at fixed bismuth amount and with varying aluminum amount. Coatings obtained with bismuth additions only were dull.

The number of dipping experiments performed to remove zinc coating on the specimens to check uniformity is shown in Table 2. The numerator of fraction is the number of experiments performed when partial removal of coating is observed whereas denominator is the number of experiments performed until the zinc coating is completely removed. The specimens obtained using the zinc bath containing 0.1 wt.% Bi and 0.025~0.05 wt.% Al showed best uniformity of coatings.

This bath composition (0.1 wt.% Bi, 0.025~0.05 wt.% Al) was tried in plant scale at a local galvanizing company in Ulsan for twelve months. About 46kg of zinc was consumed to treat 1000 kg of workpiece before the trial (12 months average). During the trial, 42 kg of zinc was consumed to galvanize 1000kg of workpiece (12 months average). As a result, four kilograms of zinc was less consumed which resulted in significant cost savings.

Amount of top dross (ash) was reduced 13 wt.%. Amount of bottom dross was reduced to 15~28 wt.%. When one touch the bottom dross by a rod, it was felt hard and thick before, now it is more soft and thinner. Oxidation rate of surface of bath after removal of ash during pulling out workpiece was low which gave good uniformity of surface color of bath. Also, it gave good luster of workpiece. The difference between maximum and minimum thickness of zinc coating was reduced. Significant drainage improvement was observed which resulted in reduction of formation of zinc icicles.

4. CONCLUSIONS

Bismuth additions improved the drainage of zinc from the specimen and prevented the zinc icicle formation significantly. The improved zinc drainage with bismuth additions deteriorated with aluminum additions. Coatings obtained with bismuth additions only were dull. Coated specimens obtained using the zinc bath containing 0.1% wt.Bi and 0.025~0.05 wt.% Al showed best uniformity. Industrial trial with bath composition (0.1 wt.%Bi, 0.025~0.05wt.% Al) showed reduction in zinc consumption, reduction of ash and dross and good luster of workpiece.

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