Investigation on the adhesion improvement of organic coatings on the surface of hot-dip galvanized steel

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Abstract. In order to solve the problem of poor adhesion of organic coatings on the surface of hot-dip galvanizing, we conducted a series of experiments to select the suitable pre-treatment method and type of the coatings. We adopted temperature shock & alternating damp heat combined test and waterproof test to simulate the service conditions, and investigated the adhesion of organic coating on the surface of hot-dip galvanizing in the wet environment. With the XPS analysis, we discussed the avoidance of formation of weak boundary layer on the hot-dip galvanizing surface by pre-treatment, and the improvement on adhesion of the organic coatings. We also proposed the pre-treatment method of coupling treatment with silane or combined alkaline washing & grinding procedures, by which the organic coating on the hot-dip galvanizing surface performed excellent adhesion and water proof ability against wet conditions.

1. Introduction
Hot-dip galvanizing steel has been widely used in industrial fields such as automobiles, electrical home appliances and construction, because of their excellent corrosion resistance [1-5]. Although the hot-dip galvanizing coating can be applied in bare state for corrosion prevention due to their dense and high thickness coating layer, in order to prolong the service life in harsh environment or provide a decorative surface, the hot-dip galvanizing steel often need coat with paints. However, it is reported many times that the coating on the surface of hot-dip galvanizing with good initial adhesion still appears typical loss of adhesion in a wet environment [1, 2], which often expressed in specific failures of coating bubbling and shedding in a large scale.

The reasons for the poor coating adhesion on hot-dip galvanizing can be ascribed as following [1]: 1) The dense and smooth galvanizing layer provides limited surface area to bond which is not good for adhesion; 2) The surface enrichment of aluminum decreased the adhesive strength to primer due to the loss of Lewis acid-base interaction at the substrate-coating interface; 3) In addition, the surface enrichment of aluminum and lead to the surface layer is responsible for the intergranular corrosion of zinc and promotes the formation of a weak boundary layer, resulting in poor bonding durability in a wet environment.

Aimed at solving this problem, many researches provide available solutions such as adjustment of hot-dip galvanizing process and chemical composition of the surface layer, optimizing the pre-treatment of paints coating and developing new type coating with strong bonding ability [3-6]. But these studies mostly focus on the improvement of coating adhesion on the galvanized steel coils applied in the field of automobiles and electrical home appliances, the designs of these hot-dip
galvanizing products take coating bonding ability into consideration at the beginning. As for the machinery manufacturing enterprises with multi-varieties and small batch products, the processing of hot-dip galvanizing mainly relies on the factories outputting their products to power and communication industrial which used in bare state. These kinds of processes consider the high thickness of galvanizing coating in primary place [7], in which aluminum and lead are added in zinc bath to improve the efficiency of galvanizing, resulting in the enrichment of impure metals to the surface layer and poor adhesion to the coatings.

In order to solve the problem of poor adhesion of organic coatings on the surface of hot-dip galvanizing, we conducted a series of experiments to select the suitable pre-treatment method and type of the coatings. We adopted temperature shock & alternating damp heat combined test and waterproof test to simulate the service conditions, and investigated the adhesion of organic coating on the surface of hot-dip galvanizing in the wet environment. With the XPS analysis, we discussed the avoidance of formation of weak boundary layer on the hot-dip galvanizing surface by pre-treatment, and the improvement on adhesion of the organic coatings. We also proposed the pre-treatment method of coupling treatment with silane or combined alkali washing & grinding procedures, by which the organic coating on the hot-dip galvanizing surface performed excellent adhesion and water proof ability against wet conditions.

2. Experiments

2.1. Samples
The samples were prepared by cutting Q235 cold-rolled sheets into 150 mm × 100 mm × 3 mm pieces. Then, the samples were degreased, pickled, rinsed, fluxed, dipped in zinc bath and quenched in water, which formed a 100 μm zinc layer after these standard hot-dip process.

The samples were degreased with acetone, then pre-treated by the method listed in Table 1. Within 8 h after pre-treatment, the samples were coated with 50 μm epoxy polyamide primer and 50 μm fluorinated acrylic polyurethane top coating.

Table 1. The method of pre-treatment before coating.

| Pre-treatment                  | Detail                                                                 |
|-------------------------------|------------------------------------------------------------------------|
| Grinding                      | Pneumatic grinding with 80 mesh sandpaper until tarnished.             |
| Sand blasting                 | Blasting with 80 mesh quartz sand under the pressure of 0.4 MPa.       |
| Phosphating                   | A domestic phosphating line was used for treatment, including degreasing, surface conditioning, phosphating and other processes. The Chemetall coupling line was adopted for treatment, including alkali washing, coupling and other processes, which was an environmentally friendly substitute technology to phosphating treatment. |
| Coupling treatment            | Immersed in Henkel Ridoline RT-1022 alkaline solution at 60°C for 2 min, then rinsed by deionized water. |
| Alkali washing                | After alkali washing treatment above and stored for 1 month, the samples were pneumatic grinded. |
| Alkali washing & grinding     |                                                                         |

2.2. Characterization

2.2.1. Adhesion test. The adhesion was determined by cross cut test according to ISO 2409:1992 and pull-off test according to ASTM D 4541-09 with a portable coating drawing tester.

2.2.2. Environmental test. In order to simulate the service conditions, the samples either served in combined temperature shock & alternating damp heat test with 10 cycles from -55°C to 70°C after that 10 cycles damp heat test which according to Chinese standards of GB/T 2423.22-2012 and GB/T
2423.4-2008, respectively, or immersed in deionized water at 40°C for 200 h for waterproof test. We took adhesion of the coating after environmental tests as wet adhesion.

2.2.3. **Surface analysis.** The chemical composition of the hot-dip galvanizing was analysed by AXIS Ultra DLD X-ray photoelectron spectroscopy (XPS). The surface roughness was measured by Mitutoyo SJ412 roughmeter.

3. **Results and discussion**

3.1. **Wet adhesion of the coating on the surface of hot-dip galvanizing**

In order to study the influence of wet environment on the coating adhesion, the samples were served in either combined temperature shock & alternating damp heat test or waterproof test. The adhesions before and after environment test were measured by drawing tester, as shown in Figure 1. Since the performance of the coating was mainly considered, the conventional grinding pre-treatment was adopted and the process referred to as following:

Degreasing → grinding → cleaning → coating the primer → curing → coating the top coating → curing.

As shown in Figure 1, initial adhesion of the coating on the surface of hot-dip galvanizing performed well of about 6.3 MPa tensile strength, but the adhesion significantly decreased after the environment tests. Especially after waterproof test, the adhesion reduced to 1.2 MPa. The phenomenon that the coating on the surface of hot-dip galvanizing inspected good was still prone to losing its adhesion in wet environments, which indicated that wet conditions played an important role in coating failure. And we got that waterproof test was an effective method in studying the failure mechanism of coatings on the surface of hot-dip galvanizing.

![Figure 1. Adhesion of the coating after environmental test.](image1.png)

![Figure 2. Adhesion of the coating with different pre-treatment.](image2.png)

3.2. **Influence of the pre-treatment on the adhesion**

According to Figure 1 the coatings showed poor wet adhesions, which could ascribe that the co-segregation of Al and Pb into the surface of hot-dip galvanizing was responsible for the intergranular corrosion of zinc and facilitated the formation of a weak boundary layer, resulting in poor bond durability in a wet atmosphere [1]. So that, we proposed several pre-treatments including grinding, sand blasting, phosphating, coupling, alkali washing and so on (Table 1), which expected to remove the impurity elements segregated to the surface and inhibit the formation of weak boundary layer.

As shown in Figure 2, the coatings on the hot-dip galvanizing showed good initial adhesions from 6.3 to 9.4 MPa with different pre-treatments, while turned up adhesion decline with various degrees after waterproof test, especially for the grinded sample. The samples treated by sand blasting and alkali washing performed good initial adhesion and limited adhesion decline after waterproof test,
which could attribute to the physical cleaning and chemical cleaning to the impurity elements, respectively. And the complete process of phosphating and coupling treatment including chemical rinsing and formation of passive films, which could not only remove the impurity elements but also provide a stable bonding layer to the coating, undoubtedly helped improve both initial adhesion and wet adhesion.

To make sure that the physical cleaning and chemical cleaning contributed to the removal of impure elements, the chemical compositions of hot-dip galvanizing were characterized by XPS with and without pre-treated by grinding, sand blasting and alkali washing, respectively. As shown in Figure 3, the surface layer of hot-dip galvanizing was composed of elements such as Zn, O, C, N, Al, Pb and P, with a complicated surface composition. The nitrogen and phosphorus could come from the fluxing of NH$_4$Cl solution and element segregation from steel, respectively, during the process of hot-dip galvanizing [8]. The aluminum and lead were the additives of zinc bath, and deservedly became the components of galvanizing coating. The carbon and oxide could accumulate during or after the process of hot-dip galvanizing. Although the contents were controlled during the process, carbon and oxide could accumulate on the surface during the storage by oxidation of zinc and then formation of basic zinc carbonate [8].

Figure 3. The XPS of hot-dip galvanizing with pre-treatment (a. survey scan, b. local zoom).

As shown in Figure 3, the composition of surface layer was still complicated after grinding, by which little improvement was made on wet adhesion of the coating. While the impure elements were significantly decreased after sand blasting and alkali washing, the nitrogen, phosphorus and lead were barely observed, and the aluminum was apparently lowered. So, the pre-treatments with sand blasting and alkali washing did work on the problem of the impurity elements segregation risking the intergranular corrosion and the formation of weak boundary layer in wet environment, which resulted in obvious improvement on wet adhesion as shown in Figure 2.

Table 2. The surface roughness of hot-dip galvanizing with pre-treatment.

| Pre-treatment                  | Surface roughness (Ra)/μm |
|-------------------------------|---------------------------|
| Blank                         | 1.28~1.41                 |
| Grinding                      | 2.53~3.14                 |
| Sand blasting                 | 5.41~7.64                 |
| Alkali washing                | 1.62~2.04                 |
| Alkali washing & grinding     | 2.48~3.26                 |

As shown in Table 2, the sample got little roughening after alkali washing, but got obvious increase in roughness with grinding and sand blasting. Comparing the sample pre-treated by alkali washing with grinding, though the coating on it got much increase in wet adhesion, the roughness of it was nearly half lesser, as roughness was very important to adhesion strength of the coating. In order to
make further improvement on adhesion, we proposed a pre-treatment combined with alkali washing and grinding as shown in Table 1, which impure elements were cleaned in washing process to contribute to long-term adhesion stability, and the rough surface with higher interfacial area was obtained in grinding process to increase the adhesion strength. As shown in Figure 2, the adhesion of the coating on sample pre-treated with alkali washing & grinding, was almost equal to that with silane coupling treatment.

3.3. Discussion on the technological process design
According to the study above, sand blasting, phosphating, coupling treatment, alkali washing and alkali washing & grinding as pre-treatment methods did work on the improvement of wet adhesion of the coating than conventional grinding in the aspect of technology, but these methods behaved differently in the aspect of applicability. Sand blasting could thin and damage the galvanizing coating which reduced corrosion resistance. Phosphating did the best on coating bonding and passivation of base metal, but it putted much burden on environment protection. While, the silane coupling treatment as an environmentally friendly substitution of phosphating process had been widely used in automobile and electric appliance industrial in recent years. And the pre-treatment of alkali washing & grinding proposed in our study also showed well potential in both coating adhesion improvement and applicability.

In domestic industrial management, the manufacturing type and processing range should be registered to government department before the factory went into operation, in the policy of processing permission range the hot-dip galvanizing production and alkali washing treatment shared the same kind of processing license, while the grinding treatment was obviously permitted in the factory with coating spraying license. As the process design proposed in our study matched well with the distribution of manufacturing type and processing range, by which we could easily cooperate to the factory with the right ability and resource, the alkali washing & grinding technological process had strong applicability and wide applicability.

Table 3. The coating system on hot-dip galvanizing.

| No. | Primer | Finish |
|----|-------|-------|
| 1# | 50 μm epoxy polyamide prime | 50 μm fluorinated acrylic polyurethane finish |
| 2# | 8 μm etch primer and then 50 μm epoxy polyamide primer | |
| 3# | 50 μm zinc phosphate epoxy polyamide primer | |
| 4# | 50 μm polyurethane primer | |
| 5# | 50 μm wet curing polyurethane primer | |

* The coating systems were verified in other tests that the primers were fitted well to finishing, unless otherwise specified, the peeling off of the coating by pull-off and cross cut tests referred to the failure between the metal and bottom primer.

As shown in Figure 4, in order to verify that the galvanizing coating pre-treated by coupling treatment or alkali washing & grinding matched well with other type coatings except epoxy polyamide primer, we measured the adhesion of the coating referring to Table 3 before and after environmental test by cross cut test. With pre-treatment of grinding, these 5 types of coatings performed well in initial adhesion, but significantly decreased after the environment test, which showed a familiar tendency to Figure 1. While with pre-treatment of coupling treatment and alkali washing & grinding, the several types of coatings showed well not only in initial adhesion but also in wet adhesion after combined temperature shock & alternating damp heat test or waterproof test. In limited comparisons, we also got that epoxy primer showed better adhesion than polyurethane primer. In general, the pre-treatment of coupling treatment and alkali washing & grinding to hot-dip galvanizing matched well with common coating systems, and these pre-treatments had good universality and potential to promote application.
Figure 4. Adhesion of the coating in Table 3 with pre-treatment (a. grinding, b. silane coupling treatment, c. alkali washing & grinding). Note: In 2# of Figure 4b, the epoxy polyamide primer was coated without coating etch primer in advance due to the unfitness between etch primer and silane film.

Based on the study, we proposed the method\textsuperscript{a} in coating on hot-dip galvanizing with excellent coating adhesion performance and good applicability:

\textsuperscript{a} Note: Making a long length short, the general process contents and details were not mentioned.

1) As for the factory with complete production equipment and batch production, we recommended,
Hot-dip Galvanizing → Complete Silane Treatment → Coating.

2) For the factory with developing equipment capability and small batch production, we recommended breaking the process into two parts, in one part metallic hot-dip galvanizing and alkali washing were finished in a metallic coating factory (or workshop section), in the other part grinding and paints coating were finished in a paints coating factory (or workshop section).
Hot-dip Galvanizing → Alkali Washing → Grinding → Coating.

4. Conclusions
We studied the adhesions of several coating systems on the hot-dip galvanizing before and after the environment tests, and the effects of pre-treatments on the adhesions, in order to solve the problem of poor adhesion of organic coatings to hot-dip galvanizing. And we discussed the avoidance of formation of weak boundary layer on the hot-dip galvanizing surface by pre-treatments with XPS analysis. Then, we got conclusions as following:

1) Although the coating with initial adhesion inspected good on the surface of hot-dip galvanizing, the adhesion could significantly decrease in a wet environment. As a result, we should pay attention to not only initial adhesion but also wet adhesion in a long-term wet environment.

2) Removing the impure elements on the surface of hot-dip galvanizing was very important to the improvement of wet adhesion of coatings, on which the pre-treatments of sand blasting, alkali washing, phosphating and silane coupling treatment did have remarkable effects.

3) Taking adhesion improvement, environmental protection and compatibility of processing resources into consideration, we recommended silane coupling treatment or alkali washing & grinding treatment as the pre-treatment on hot-dip galvanizing, which could effectively guarantee the adhesion performance of organic coatings.
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