THE PARAMETERS AFFECTING ADHESION OF HDG COATING

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Abstract

The paper shows the evaluation of delamination of HDG coating. The HDG coating adhesion was evaluated by impact test and by pull-off test. The effect of substrate steel chemical composition, metallurgical conditions and other parameters influencing the quality of zinc coating, mainly the intermetallic phases, are described. The silicon content in aluminium-killed steel was identified as crucial factor for tested samples. The result of adhesion test corresponds to structure of zinc coating.

Keywords: HDG coating, adhesion, steel chemical composition, intermetallic phases

1. INTRODUCTION

Hot-dipped galvanized steel is a widely used material in numerous applications due to its corrosion-resistance and relatively inexpensive cost. Zinc coating provides corrosion protection to the substrate steel by forming a barrier against the environments and a galvanic effect due to the fact that zinc is anodic to iron and behaves as sacrificial material at discontinuities in the coating. The protection period of a zinc coating depends mainly, for a given atmospheric conditions - corrosivity categories, on the thickness of the applied coat in accordance with EN ISO 9224 and EN ISO 14713 [1 - 3]. A number of defects may occur on hot dip galvanized construction elements and, some of them are critical in terms of their influence on corrosion protection properties [4].

The qualitative parameters of the standard hot dip galvanized coating are specified in EN ISO 1461 [5]. They are appearance of coating, its thickness, continuity and adhesion. The appearance of the hot-dip galvanized coating can vary from piece to piece, and even section to section of the same piece. Common appearances for hot-dip galvanized steel immediately after galvanizing include bright and shiny, spangled, matte grey, and/or a combination of these. The thickness of coating is determined mainly by the nature and thickness of the steel. The typical thickness is between 35 and 100 µm. It is at the equivalent of 85 µm minimum for steel > 6 mm thick according to EN ISO 1461. Heavy hot dip galvanized coatings greater than 250 µm thick, may have brittle tendencies.

Adhesion between zinc and steel generally does not need to be tested as adequate bonding is characteristic of the intermetallic Zn-Fe layers forming a metallurgical bond between the zinc and the underlying steel. Typical galvanized coating microstructure consisting of three alloy layers: γ phase (75% Zn, 25% Fe), δ phase (90% Zn, 10% Fe), ζ phase (94% Zn, 6% Fe) and a top layer of pure metallic zinc - η phase. For most hot-rolled steels, the zinc-iron alloy portion of the coating will represent 50 - 70% of the total coating thickness, with the free zinc outer layer η accounting for the balance. These layers differ in hardness too, which may affect the resistance of HDG coating against mechanical stresses. Typically, the γ, δ, and ζ layers are harder than the underlying steel (250, 244 and 179 HV). The hardness of these inner layers provides exceptional protection against coating damage through abrasion. The η layer of the galvanized coating is quite ductile (70 HV), providing the coating with some impact resistance.

Testing for adhesion is not necessarily a true measure of the adhesive strength of the metallurgical bond between the hot dip galvanized coating and the base steel, but it does serve as an indicator of the adhesion properties of the coating. Localised delamination/flaking can occur with zinc coatings if there are subject to impact or point pressure. For zinc coated steel the process of interface fracture and coating delamination is very complex, because prior to fracture extensive plastic deformation in the zinc coating and the steel substrate occurs [6 - 10]. This leads to non-uniform stress distributions within the interface zone.

2. EXPERIMENTAL

2.1. Specification of tested samples

Several pieces of galvanized steel structures - samples - were experiencing a problem with the galvanized coating adhesion (**Figure 1**). These pieces have steel thickness 6, 8 and 10 mm and differ in few parameters of zinc coating summarised in **Table 1**.

Table 1 Characterization of zinc coating on samples

sample	average coating thickness [µm]	appearance	adherence	microstructure of coating
A	95	silvery bright, zinc spangles	excellent	typical structure - 4 phases γ, δ, ζ, η
B	155	matte grey, sometimes granular	poor	phase η is missing, phase δ is very low
C	207	pale grey	poor	mixed structure - 4 phases γ, δ, ζ, η

Figure 1 Example of delamination of HDG coating on construction´s elements

Cross sections of the galvanized coatings were prepared in the studied areas for subsequent conventional metallography inspection and examined by optical microscopy. The specimens were etching with a 1% nital solution revealed the existing microstructure of zinc coating. Microstructures of zinc coating of evaluated samples are shown in cross sections in **Figure 2**:

- sample A - typical structure with all 4 phases where η phase is uniform and creates ca 30% of total zinc coating thickness; phase δ is relative thick
- sample B - phase δ is very low; there is no phase η; the dominant phase is ζ creating large and sharp crystals
- sample C - there are 4 phases with so call mixed structure; phase η is partly defunded into phase ζ; phase ζ creates large and sharp crystals

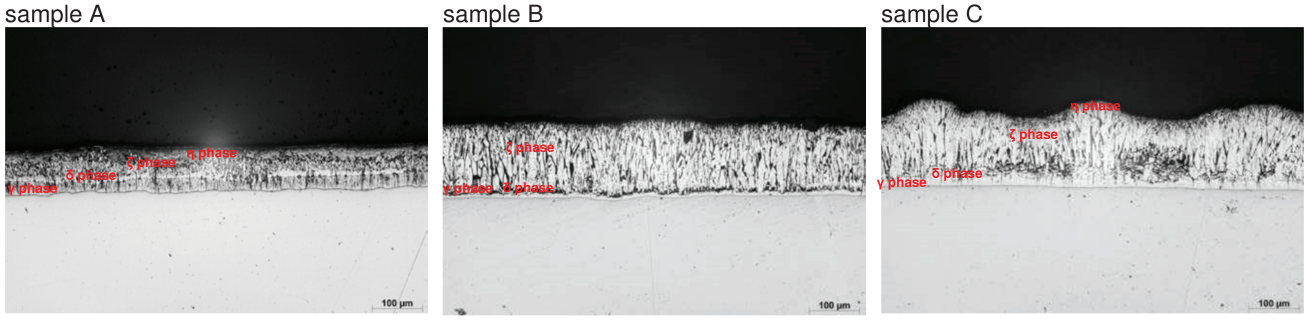

Figure 2 The zinc coating structure on samples

On areas with partial delamination of the zinc coating, cross sections of zinc coated steel were prepared to determine the location and extent of the interface cracking and the crystallographic orientation of the delaminated zinc grains - **Figure 3**. There is evident the delamination of zinc coating occurred between zinc coating and steel surface or between δ phase and ζ phase layers and there is also evident that the residual zinc coating layer is deformed by stress affecting in minimum 2 directions.

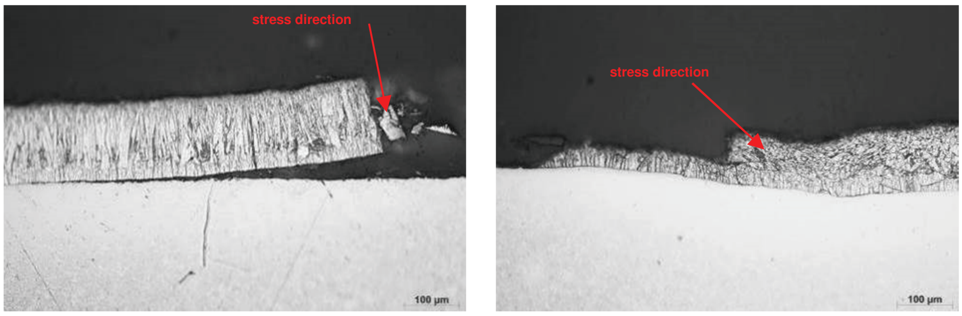

Figure 3 The delamination of HDG coating on samples from site

2.2. Measurement of adhesion of hot-dip galvanized coating

In accordance with EN ISO 1461, adhesion between the zinc coating and the substrate does not normally need to be tested, because zinc coatings have adequate adherence for resisting mechanical impacts during normal handling operations and use without spalling or flaking off.

The methods routinely employed, such as the cross-hatch test, hammer test specified in ASTM A123 [11] and the impact tests in accordance with DIN 50978 [12], are restricted to a maximum coat thickness of approximately 150 µm, and provide only qualitative information. Moreover, these methods mainly assess the ductility and sensitivity to scaling of zinc coatings rather than their adhesion capability.

The modified test method used for organic coatings in accordance with EN ISO 4624 [13] allows the adhesion of zinc coatings to be determined with statistical reliability up to 45 MPa. These characteristic adhesion values indicate the tensile strength or uplift resistance of zinc coatings, which, in conjunction with the (adhesive or cohesive) failure patterns, enable the assessment of their adhesion capacity. With the exception of Sebisty steels, measured average values for the adhesion of zinc coatings in accordance with EN ISO 1461 are generally greater than 20 MPa. The values for Sebisty steels vary from 10 to 18 MPa.

Results of impact and pull-off tests of samples in **Table 2** and on **Figure 4** show that pull-off test is not suitable for testing the adhesion of HDG coating as the affecting stress is different from real stress of coating in orientation and distribution. During the pull-off test the mechanical stress is applied on the coating with tensile force uniformly increasing and uniformly distributed on all surface of pull-off test cylinder. Stresses affecting anywhere in coating are 3D distributed. Impact stress application with defined impact energy in 90° to coating surface in relative short line so it is 2D distributed. In case of coating with low adhesion the main damaging mechanisms depend on the different mechanical behaviour of the intermetallic phases and on their thickness. For all the investigated coating conditions, radial cracks are observed on **Figure 5**. They initiate corresponding to the γ phase and propagate up to the ζ–η interface. The coating thickness increase implies both an increase of the importance of the cracks in δ and ζ phases and the presence of cracks at ζ–δ interfaces. The character and propagation of cracks looks similar to real delamination cracks (**Figure 3**).On **Figure 5** there is seem the difference in crack propagation according to zinc coating structure on sample B and C.

Table 2 Results of adhesion tests

<table>
<tr><th rowspan="2">sample</th><th colspan="2">pull-off test</th><th rowspan="2">impact test</th></tr>
<tr><th>strength (MPa)</th><th>character</th></tr>
<tr><td>A</td><td>12.4</td><td rowspan="3">adhesion failure between adhesive and test cylinder</td><td>excellent</td></tr>
<tr><td>B</td><td>16.1</td><td>total loss of adhesion</td></tr>
<tr><td>C</td><td>14.8</td><td>acceptable</td></tr>
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sample A sample B sample C

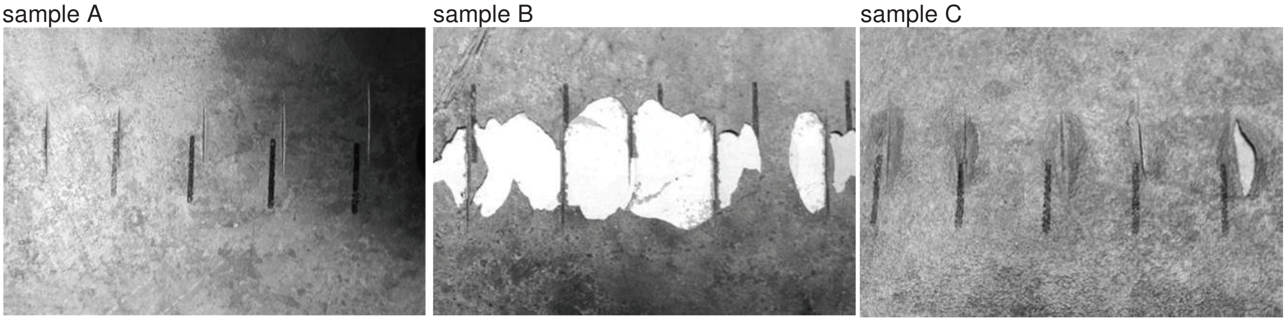

Figure 4 The results of impact test on samples

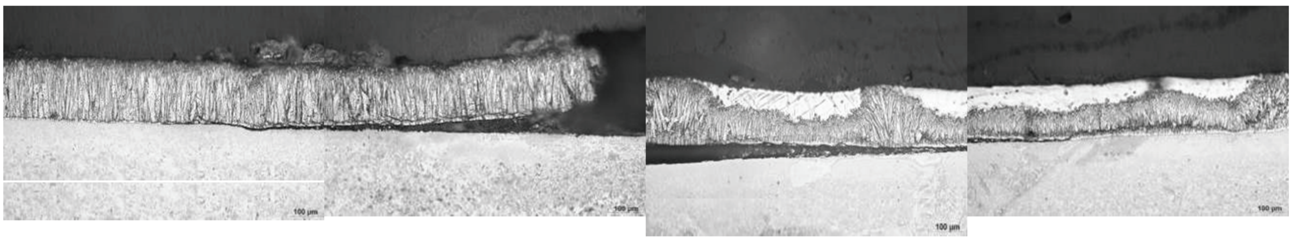

Figure 5 The delamination of HDG coating after impact test on sample B (left) and sample C (right)

2.3. Steel chemical composition

The chemical composition of substrate steel of all tested samples had been analyzed by EDAX method. The results are in **Table 3** and show the different composition of substrate steel in silicon (Si) and aluminium (Al) content affecting the quality of HDG coating.

Table 3 Steel chemical composition (wt. %)

sample	Al	Si	P	Mn	Fe
A	0.08	0.07	0.02	0.84	98.99
B	0.07	0.25	0.02	1.55	98.12
C	0.03	0.22	0.03	1.61	98.10

2.4. Measurement of zinc coating microhardness

The coating microstructure also indicates the hardness of each layer. Typically, the γ, δ, and ζ layers are harder than the underlying steel. The hardness of these inner layers provides exceptional protection against coating damage through mechanical stress. The η layer of the galvanized coating is quite ductile, providing the coating with some impact resistance. The measurement of zinc coating hardness was performed by Vickers method with BuehlerMet 1105 instrument. The results are in **Table 4** and **Figure 6**. The results show that the hardness of ζ phases is practically the same for tested samples and in case the low value the phase η was measured (57 HV for sample B).

Table 4 Microhardness measurement

sample	hardness (HV 0.1)		
	1	2	3
A	105	124	113
B	85	100	57
C	97	96	85

typical values sample A sample B sample C

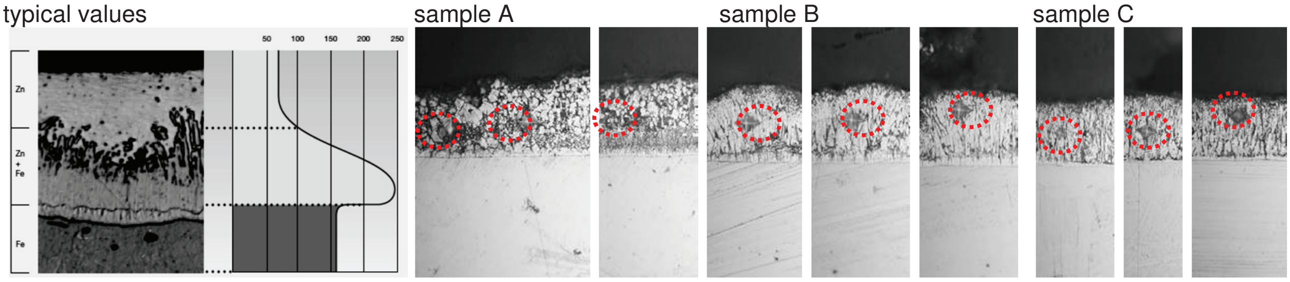

Figure 6 The results of microhardness measurement on samples

3. DISCUSSION OF RESULTS

During steel production, silicon or aluminium is added to remove oxygen. These steels are known as "killed steels". Since the content of silicon (Si) affects the hot dip galvanizing reaction, the silicon content should always be taken into consideration for steels that will be galvanized. The recommended silicon quantity for steel to be galvanized is either less than 0.04 wt. % or between 0.15 wt. % and 0.25 wt. %. Steels outside these ranges are considered reactive steels and can be expected to form zinc coatings thicker than average. Aluminium-killed steels suitable for galvanizing have low silicon content, below 0.03 wt. %. Silicon-killed steels with silicon content above 0.14 wt. % works well in galvanizing, but give a thicker coating than aluminium-killed steels. The phosphorus content of the steel also influences on the reactivity, especially for cold rolled steels. Other alloying elements in the steel have no major influence on the coating.

Tested samples have different chemical composition of substrate steel:

- sample A is aluminium killed steel with low silicon content and so it behaves well during galvanising. The zinc coating has adequate appearance, thickness and there is no problem with coating adhesion even in case of mechanical stress.
- sample B is also aluminium killed steel but it contain high amount of silicon too. This type of steel should be avoided for hot-dip galvanizing. In a conventional zinc bath the reaction between this type of steel and zinc is very strong and the coating becomes thick and irregular, often with poor adherence. The zinc coating is grey.
- sample C is silicon killed steel with some amount of aluminium, but its silicon content should preferably be in the range 0.15 - 0.22 wt. % silicon. However, the coating will be thicker than is required by the standard.

4. CONCLUSION

Batch hot-dip galvanizing has been the most commonly used method of protecting steel products against corrosion. Hardness, ductility, and bond strength combine to provide the galvanized coating with unmatched protection against damage caused by rough handling during transportation to and/or at the job site as well as during its service life. Although the hot-dip galvanizing procedure is recognized to be one of the most effective techniques to combat corrosion, cracks can arise in the intermetallic layer. These cracks can affect the life of the coated material and decrease the lifetime service of the entire structure.

The failure analysis of galvanized samples with delaminated HDG coating includes thickness measurements of the coatings, metallography microstructure analysis of coatings, analysis of chemical composition of base steel, adhesion and microhardness measurements. Depending on the steel chemistry, zinc coatings vary in appearance, thickness, structure and adhesion. Standard EN ISO 1461 does not include any recommendation in respect to aluminium killed steel. As the difference between suitable and non- suitable steel for galvanising is very low and as it vary in hundredths of per cents, it is very difficult to control the steel quality before galvanising.

ACKNOWLEDGEMENTS

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REFERENCES

[1] ISO 9224 Corrosion of metals and alloys - Corrosivity of atmospheres - Guiding values for the corrosivity categories, 2012

[2] EN ISO 14713 Zinc coatings - Guidelines and recommendations for the protection against corrosion of iron and steel in structures, 2009

[3] GEIPLOVA H., KREISLOVA K., MINDOS L., TUREK L., Evaluation of long-term exposed structures and their maintenance, Corrosion and Surface Treatment in Industry, Material Science Forum, Vol. 844, ISBN 978-3-03835-525-0, 2016, pp. 79-82

[4] GEIPLOVA H., KREISLOVA K., TUREK L., BARTAK Z., The application of metallography for evaluation of hot dip zinc coatings, (in press)

[5] EN ISO 1461 Hot dipped galvanized coatings on fabricated iron and steel articles - Specifications and test methods

[6] MICHAL G.M., JANAVICIUS P.V., PAIK D.J., FRCY K.R., In: *Galvatech '04 Conference Proceedings*, 2004, p. 517, April 4-7, Chicago, USA.

[7] SONG G.M., SLOOF W.G., PEI Y.T. , De HOSSON J.Th.M., Interface fracture behavior of zinc coatings on steel: Experiments and finite element calculations, *Surface & Coatings Technology*, 201, 2006, 4311-4316.

[8] SONG G.M., VYSTAVEL T., van der PERS N., De HOSSON J.Th.M., SLOOF W.G., Relation between microstructure and adhesion of hot dip galvanized zinc coatings on dual phase steel, *Acta Materialia*, 60, 2012, 2973-2981.

[9] KIM S.R., NAIRN J.A., Fracture mechanics analysis of coating/substrate systems. Part I: Analysis of tensile and bending experiments, *Engineering Fracture Mechanics*, 65, 2000, 573-593.

[10] KIM S.R., NAIRN J.A., Fracture mechanics analysis of coating/substrate systems. Part II: Experiments in bending, *Engineering Fracture Mechanics*, 65, 2000, 595-607.

[11] ASTM A123 Standard Specification for Zinc (Hot-Dip Galvanized) Coatings on Iron and Steel Products

[12] DIN 50978 Prüfung metallischer Überzüge; Prüfung des Haftvermögens von Zinküberzügen, die nach dem Schmelztauchverfahren hergestellt wurden

[13] EN ISO 4624 Paints and varnishes - Pull-off test for adhesion