ANALYSIS OF THE HYDROGEN CONCENTRATION IN THE HOT-DIP GALVANIZED AND ELECTROPLATED PRODUCTS MADE OF HIGH STRENGTH STEEL

WĘGRZYNKIEWICZ Sylwia[1], SOZAŃSKA Maria[2], MULEC Jarosław[1], GAŚ Paweł[1], KRAWCZYK Przemysław[1], HAJDUGA Maciej[3]

[1] BELOS - PLP S.A., Bielsko-Biała, Poland, EU
[2] Silesian University of Technology, Faculty of Materials Engineering and Metallurgy, Katowice, Poland, EU
[3] Academy of Technology and Humanities, Bielsko-Biała, Poland, EU

Abstract

The results of the hydrogen concentration measurements in selected products, made of steel grade 41Cr4, are presented in the following paper. The reason for this project was the failure of the tower structure and the suspicion of brittle fracture caused by hydrogen in one of the hot-dip galvanized products made of steel grade 41Cr4, found in the wreckage of the tower. Due to the fact that the opinion was formulated on the basis of the results of the hydrogen content measurements in broken products, (20 ppm) it was decided to examine this problem more closely. The hot-dip galvanized and electroplated metal elements were subjected to a hydrogen content test. Two types of samples: with and without zinc coating were prepared for analysis. The analysis was performed using an elemental analyser, the LECO ONH836. Diversification of hydrogen content on the sample cross-section was revealed after the profile of its contents was known. It has been found that a high hydrogen content was observed only and exclusively inside the zinc coating. This means that the presence of the Zn coating in the sample affects the accuracy of the measurement of the hydrogen content and can lead to erroneous conclusions about the hydrogen embrittlement or hydrogen charging of steel. The results of the hydrogen concentration in each case should be considered carefully as the total concentration of the hydrogen content is measured, and not only the hydrogen diffusion responsible for the occurrence of hydrogen embrittlement.

Keywords: 41Cr4 steel, measurement of hydrogen content, hot-dip galvanizing, electroplating

1. INTRODUCTION

The development of technology causes growth in the demand for materials with specific utility functions. Produced goods have to meet growing safety and functionality requirements, and at the same time reduce production and utilization costs.

The higher the tensile strength or hardness of the fastener, the greater the risk of hydrogen embrittlement. High strength steels which have a tensile strength (Rm> 1000 MPa) and hardness above 39 HRC (380HV) [1] or 34 HRC (340HV) acc. to [2] are the most susceptible to the effects of hydrogen embrittlement.

Proper surface preparation of metal elements made of high strength steel before HDG is a difficult and complicated process. There are a lot of standards presented in the requirements and recommendations for HDG of high strength steel galvanizing. According to EN 10684, parts heat treated or work hardened to a hardness of ≥ 320 HV must be cleaned using an inhibited acid, alkaline or mechanical process [3]. Guidelines is given by German standad „Richtlinie für die Herstellung feuerverszinkter Schrauben" [4] indicate the inhibited acid concentration in the range from 8 to 15%. The pickling time should be no longer than 30 minutes for fasteners in class 8.8 and 15 min. for class 10.9. Recommended pickling parameters are extremely important to meet.

During the pickling of steel in HCl, hydrogen *„in statu nascendi"* is released. It is moved into the steel and is absorbed on the surface of the cleaned metal element. Hydrogen absorbed on the surface is partially

evaporated during the galvanizing process (at 460 °C). A part of hydrogen is trapped in the Zn coating and it is released later, within a few days after galvanizing [5,6].

The hydrogen concentration in metals and alloys has an unfavorable impact on their physical, mechanical and electrochemical properties. Reduction of yield strength and brittle fracture are caused by the hydrogen content even at the level of a few ppm. Non-metallic inclusions, grain strongly defected or high hardness phase initiate crack. The changes in the microstructure of the steel in the form of cracks, as well as delamination and blisters with hydrogen or methane, which can cause the total destruction of the structure already below the yield strength, even the static load of the structure [1,5-9]. It was stated that the higher hydrogen concentration in steel, the more intense its destruction is. Hydrogen in metallic material, especially in deformed material, may be present not only in the form of atoms located in interstitial gaps of crystal structure, but it also may be connected with varied forms of structural defects [5-9].

The measurement of hydrogen content in steel is difficult due to very low levels of diffusible hydrogen present in steel and the possibility of contamination from external sources in the analysis. It should be noted that during the test the sample is melted [7,9,10]. Measuring the total hydrogen concentration in steel to prove the presence of hydrogen embrittlement is inadequate. The major portion of the hydrogen atoms is trapped at dislocations, at the matrix/fiber interface (eg. carbides, nitrides, non-metallic inclusions) and on grain boundaries and does not necessarily partake in the embrittlement of the steel [10]. An extremely important procedure before the measurement of hydrogen content is thoroughly remove the zinc coating. Zinc coating on steel and hydrogen interactions is presented in **Figure 1**. It is shown that the hydrogen which interacted with the zinc remained in the intermetallic layer between the zinc and the steel. The hydrogen in the Zn coating is stored in the different forms. Some hydrogen is absorbed into the metallic layer as H^+ or trapped in metallic particles as H_2. To determine the diffusible or the total amount of hydrogen in steel, the zinc coating must be carefully removed because the contaminants that interact with zinc can have a negative influence on actual hydrogen concentration [9,11].

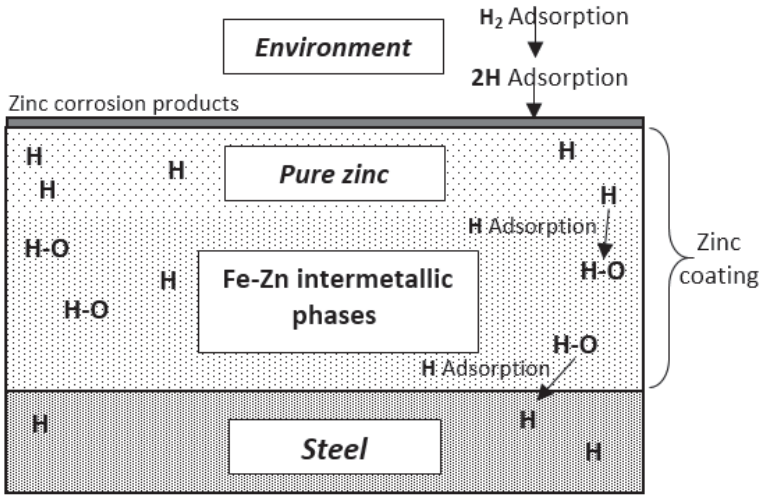

Figure 1 The content of hydrogen in the zinc coating and steel - the interaction [9]

This means that the presence of the Zn coating in the sample affects the accuracy of the measurement of the hydrogen content and can lead to erroneous conclusions about the hydrogen embrittlement of steel. The above is proven at work [11]. The hydrogen concentration in a 41Cr4 steel sample taken from a U-bolt product with Zn coating was at several tens of ppm while the hydrogen content in the steel did not exceed 1 ppm (**Figure 2**).

Moreover, it has been proven that the use of shot blasting before HDG and elimination of pickling in HCl does not provide the results of hydrogen concentration at the level of 1-2 ppm if sample with Zn coating is analysed [11].

Figure 2 The hydrogen concentration results for samples taken with Zn coating (31 ppm) and without coating (0.37 ppm) [11]

The aim of this study was the evaluation of the hydrogen concentration in hot-dip galvanized and electroplated elements made of steel grade 41Cr4.

2. THE HYDROGEN CONCENTRATION TEST

2.1. The objects of analysis

The analysis was focused on elements made of grade 41Cr4 steel (0.38-0.45 %C, ≤ 0.30 %Si, 0.60-0.90 %Mn, ≤ 0.035 %P, ≤ 0.035 %S, 0.0-1.2 %Cr, ≤ 0.3 %Ni, ≤ 0.25 %Cu, ≤ 0.1 %Mo, ≤ 0.05 %V wg EN 10083-3: 2006). A fastener (hot line socket clevis) and eye bolts protected by HDG and a bolt Tr30x3 after electroplating and passivation of Cr^{3+} were selected for the analysis. The objects of analysis were shown in **Figure 3**.

In order to assess the impact of the intensive removal process of the Zn coating on hydrogen content, eye bolts were subjected to regalvanizng. Different times of keeping the eye bolts in the HCl solution were used: 1 h and 42 hrs. The characteristics of the test objects are shown in **Table 1**.

Table 1 Division of material for hydrogen content testing

Method of galvanizing	Description / Sample designation		Technological operations
HDG acc. to EN ISO 1461:2009	Fastener	**Ł**	- Cast steel shot, GL40, t = 20 min. - HCl (12 %) + inhibitor, 10 min. - HDG in temp. 457 °C and centrifurging
	Eye bolt	**S1**	- Cast steel shot, GL40, 20 min. - HCl (14 %) + inhibitor, 10 min. - HDG temp. 457 °C and centrifurging - removing Zn coating in HCl (9.7 %) + inhibitor, 1 h - HDG in temp. 457 °C and centrifurging
		S42	- Cast steel shot, GL40, 20 min. - HCl (14 %) + inhibitor, 10 min. - HDG temp. 457 °C and centrifurging - removing Zn coating in HCl (9.7 %) + inhibitor, 42 hrs. - HDG in temp. 457 °C and centrifurging
Electroplating acc. to EN ISO 4042:2001	Bolt Tr30x3	**T**	- alkaline degreasing, temp. 65°C, - 10 % HCl + inhibitor, - galvanization in low acid chloride Zn (zinc chloride, potassium chloride) boric acid baths, 27 °C, pH 5.2, - passivation of Cr^{3+}

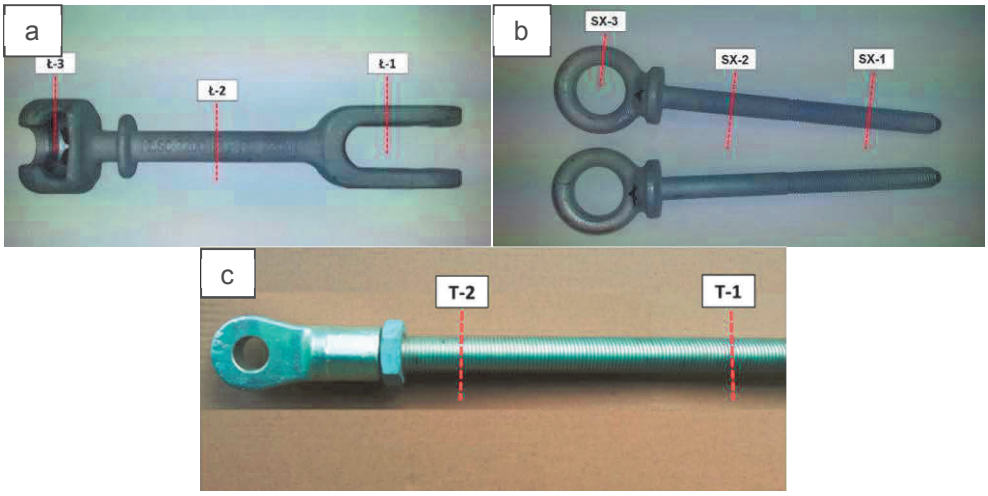

Figure 3 The objects of analysis: a) fastener Ł, b) eye bolts SX, c) bolt Tr30x3; Ł1, Ł2, Ł3, SX-1, SX-2, SX-3, T-1, T-2 sampling points for the hydrogen content test, X = 1 or 42 - time of removal of Zn coating from eye bolts in HCl

2.2. Material for the research and methodology

Samples weighing approximately 1 gram were taken for the hydrogen content test. Two types of samples: samples without Zn coating (**Figure 4a**) and samples with Zn coating (**Figure 4b**) were prepared for analysis.

A profile of hydrogen concentration was made on a cross-section of the selected samples, from surface to interior. Samples designed for this purpose were cut at different distances from the item surface, in accordance with the diagram presented in **Figure 4c**.

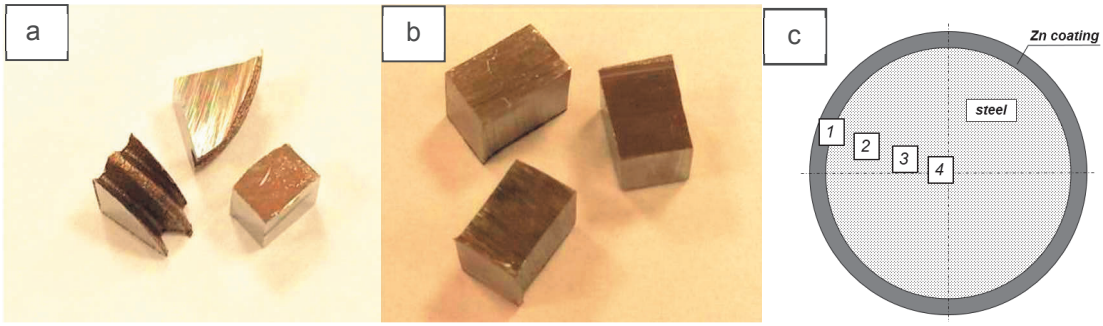

Figure 4 Test samples: a) with Zn coating, b) without Zn coating, c) indication of points for measuring the hydrogen content on a cross-section of the sample (1 - steel sample with Zn coating, 2,3,4 - steel samples without Zn coating

The tested material was intensively cooled with water during cutting in order to minimize the escape of hydrogen from the material. After cutting, the samples were subjected to cleaning in an ultrasonic washer with acetone twice for 3 minutes, each time, the acetone was replaced with a fresh batch.

Then, a determination of the hydrogen content of the samples prepared in this way were done by a LECO ONH836 elemental analyser. The measurement of the hydrogen content in the samples was preceded by a blank test (the analysis of the helium and the crucible). Before, during and after measuring the hydrogen content in the samples, the hydrogen content in the test samples was compared to the hydrogen content in the control samples. Each measurement was performed three times, and then an average value was calculated with a standard deviation of the obtained results.

An elemental analyser LECO ONH836 can be used to analyse oxygen, nitrogen and hydrogen in a wide range of concentrations from 0.1 ppm upwards. During analysis of the concentration of oxygen, nitrogen and hydrogen, the sample of a nominal weight of approximately 1 g is placed in a graphite crucible, where it is melted, which results in the release of gases contained therein. Oxygen immediately reacts with graphite in the crucible to form CO and CO2; nitrogen and hydrogen are released in particle form. After that, these gases are transported in a flow of helium of a minimum purity of 99.999% in the direction of the catalyst, where oxidation of CO into CO_2 and H_2 into H_2O occur. Hydrogen is measured as H_2O on the IR detector. Oxygen content measurement is performed separately on the CO detector and twice on the CO_2 detector (before and after passing through the catalyst), which ensurs the accuracy of measurement. After removing H_2O and CO_2 from the analytical gases, their loss is automatically compensated for, followed by measurement of nitrogen content on the TCD thermo-conductive detector.

3. RESULTS OF THE RESEARCH

The results of the hydrogen content in samples with and without Zn coating are presented in **Table 2**. The hydrogen concentration profile in the fastener and the Tr30x3 bolt from its surface to its interior are presented in **Table 3**.

Table 2 Concentration of hydrogen in the tested samples with and without Zn coating, [ppm]

Description	Sample designation	Hydrogen concentration, ppm	
		Samle with Zn coating	Sample without Zn coaing
FASTENER	Ł-1	0.80 ± 0.47	
	Ł-2	0.35 ± 0.18	7.95 ± 0.53
	Ł-3	1.28 ± 0.23	
EYE BOLTS	S1-1	0.49 ± 0.25	8.15 ± 1.32
	S1-2	0.18 ± 0.17	
	S1-3	0.57 ± 0.28	
	S42-1	0.29 ± 0.10	3.95 ± 0.25
	S42-2	0.63 ± 0.04	
	S42-3	0.64 ± 0.09	
BOLT Tr30x3	T-1	2.49 ± 0.36	23.11 ± 0.94
	T-2	2.19 ± 0.23	

Table 3 Hydrogen concentration profile in fastener (Ł-2) and bolt Tr30x3 (T-2) from its surface to its interior (1 - steel sample with Zn coating, 2,3,4 - steel sample without Zn coating), [ppm]

Description	Sample designation	Hydrogen concentration, [ppm]	
		Fastener Ł-2 (after HDG)	Bolt Tr30x3 T-2 (after Electroplating)
Steel sample with Zn coating	1	3.92 ± 1.04	20.37 ± 1.47
Steel sample without Zn coating	2	0.89 ± 0.52	2.62 ± 0.61
	3	0.66 ± 0.29	2.27 ± 0.22
	4	0.71 ± 0.25	2.11 ± 0.24

4. RESULTS DISCUSSION

The standard hydrogen content in steel grade 41Cr4 is 1-2 ppm. On the basis of the results and with regard to [11] it can be concluded that hydrogen content is strictly dependent on the specific sampling point. Samples containing Zn coating have a higher hydrogen content than steel samples without Zn coating both in the case of HDG and electroplating.

In spite of intensive chemical treatments such as 41Cr4 steel (eye bolts, S1 and S42), the excess hydrogen content in steel (above 1ppm) was not measured. High hydrogen concentrations were determined only in samples covered in Zn coating. Moreover, eye bolts, which were kept longer in the acid bath, 42 hours have about 52% less hydrogen than those pickled for less than 1 hour (**Table 2**).

For samples taken from the bolt Tr30x3, the hydrogen concentration was 23 ppm for the samples taken with the Zn coating. For samples without Zn coating, 2 ppm hydrogen was measured.

Diversification of hydrogen content on the sample cross-section was revealed after the profile of its contents was known, for both fastener Ł after HDG and bolt Tr30x3 after electroplating. The highest amount of hydrogen was determined for sample 1 (**Figure 4c**) taken with Zn coating. For sample Ł-2-1, it was 4 ppm, for sample T-2-1, it was 20 ppm. The hydrogen content in samples without Zn cut from a steel core did not exceed 1 ppm for the fastener and 2 ppm for the bolt Tr30x3.

Compared to the results obtained for hot galvanized and electroplated samples, higher hydrogen concentrations were measured for samples with electroplated Zn coating. Taking into account previous test results [11], it was found that the measured hydrogen concentration for the Tr30x3 bolt was comparable to the results for U-Bolts UK-1 and UD-1 (**Figure 5**). In both cases, the results may have been affected by passivation. It was found [11] that the Zn coating on UK-1, UD-2 products was coated with white rust. In contrast, in the present case, the passivity of Cr^{3+} was undoubtedly influenced by the T-1 sample.

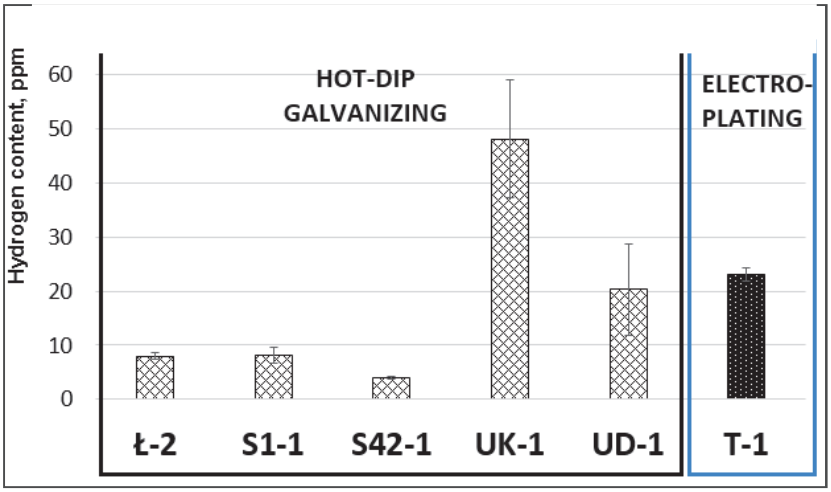

Figure 5 Hydrogen content in samples covered hot-dip galvanized and electroplated coatings, ppm [11]

The measurement of hydrogen content in steel is difficult due to very low levels of diffusible hydrogen present in steel and the possibility of contamination from external sources in the analysis. It should be noted that during the test the sample is melted. All hydrogen, even that which has been trapped, is released in this way. Therefore, the results of the hydrogen concentration in each case should be considered carefully as the total concentration of the hydrogen content is measured, and not only the hydrogen diffusion.

5. CONCLUSIONS

Based on the presented test results and conducted analysis, the following conclusions can be drawn:

1) The presence of the Zn coating in the sample affects the accuracy of the measurement of the hydrogen content and can lead to erroneous conclusions about the hydrogen embrittlement or hydrogen charging of steel.

2) Hydrogen marked in products with Zn coating on the level of several ppm will have no impact on the deterioration of steel mechanical properties and hydrogen embrittlement.

3) No higher hydrogen content in zinc coating of samples subjected to intensive chemical treatment was reported as compared to samples whose time of contact with etching acid was longer. The level of hydrogen in steel did not exceed 1 ppm in each case.

REFERENCE

[1] BRAHIMI S., *Fundamentals of hydrogen embrittlement in steel fasteners*, IBECA Technologies Corp., Québec 2014, 23 p.

[2] EN ISO 14713-2:2010 Zinc coatings - Guidelines and recommendations for the protection against corrosion of iron and steel in structures Part 2: Hot dip galvanizing

[3] ISO 10684:2004 Fasteners -- Hot dip galvanized coatings

[4] Richtlinie für die herstellung feurverzinkter Schrauben, Deutscher Schraubenverband EV, July 2009

[5] KUKLÍK, V., KUDLACEK, J., *Zarove zinkowani*. Praha: Asociate ceskych a slovenskych zinkoven, 2014, 324 p.

[6] SCHULTZ, W., THIELE, M., Cynkowanie ogniowe jednoskowe. Materiał - Technologia - Powstawanie powłoki- Właściwości- Błędy, Bad Saulgau: Eugen G. Leuze Verlag KG, 2012.

[7] SOZAŃSKA, M. *Niszczenie wodorowe typu "rybie oczy" wybranych stali dla energetyki*, Gliwice: Politechnika Śląska, 2006, 156 p.

[8] KUKLÍK, V., Post on the issue of safety of steel structures of hot dip galvanized structural components. *Procedia Engineering*, 2012, vol. 40, pp. 241-246

[9] NONHLANGABEZO M., *Determination of diffusible and total hydrogen concentration in coated and uncoated steel*, doctoral thesis, University of Duisburg-Essen, 23.09.2010

[10] STUMPF, WE. Placing hydrogen embrittlement (HE) of fasteners into perspective, *Hot Dip Galvanising Today*, 2012, vol. 9, no 1, pp. 10-13

[11] SOZAŃSKA, M., WĘGRZYNKIEWICZ, S., KIEŁBUS, A., MOŚCICKI, A., HAJDUGA, M. Analysis of the hydrogen concentration in the products made of steel grade 41Cr4. *Ochrona przed korozją,* 2017, vol. 60, no. 4, pp. 96-10