

Hydrogen measurement of Zn-coated cold rolled strip

ESTEP Focus Group **Transport and Mobility**¹, March 2022, with main contributions from:

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1. Background

Due to the demanding climate protection goals, lightweight solutions are essential for the transport sector. Currently the risk of hydrogen embrittlement (HE) is one factor restricting the extensive use of cold rolled UHSS-grades in automotive applications.

In recent years, comprehensive studies have been conducted on the evaluation of hydrogen embrittlement in the field of thin sheet grades for the automotive industry. Nevertheless, despite significant progress, further evaluation of existing measurement and testing procedures and the development of new approaches are still necessary.

2. State of the art

The sensitivity to HE is often characterized by combining mechanical tests in combination with the evaluation of the hydrogen content, focusing on the so-called “diffusible” hydrogen. Therefore, it is essential to evaluate and compare different results obtained by means of TDA/TDS (thermo desorption analysis/thermo desorption spectroscopy) by different labs. In current active standards, often compiled for validating cold cracking after welding operations, hydrogen is labelled as diffusible when it is measured in the temperature range between room temperature and 400°C, consisting of lattice hydrogen and weakly trapped hydrogen e. g. at dislocations, grain boundaries, etc. [ISO 16573:2015, DIN EN ISO 3690:2012, Handbuch für das Eishüttenlaboratorium Band 2 Teil 2, ASTM F519-18, ASTM F1624-12, ASTM G129:1988] Until now a detailed description for handling and preparation of zinc-coated samples is still lacking. Further references of diffusible hydrogen will be denoted by simple hydrogen.

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3. Aim of the collaborative work

The topic “hydrogen embrittlement” (HE) within ESTEP is exclusively focusing on cold rolled and zinc-coated high strength steel materials used or designed for automotive applications.

4. Experimental procedure

Every preparation step can potentially change the hydrogen content in the steel, leading to additional deviations of the result. Therefore, to reduce the scattering all initial preparation steps (hydrogen charging, Zn-coating and distribution) were performed by one single lab. A bilateral comparison of the results was conducted on identical parts of the same sample.

4.1. De-coating & Degassing

Investigations were performed on an industrial, hot dip Zn-coated DP1000 grade with a thickness of 1.5 mm. Initial samples of 100 mm x 100 mm were stamped from the same metal sheet and de-coated in 20% HCl with 5 g/l Hexamethylenetetramine acting as inhibitor. Afterwards the samples were cleaned and stored in an exicator for 24 hours to reduce the hydrogen content. The residual hydrogen content of the samples after this process was about 0.05 ppm.

4.2. Charging & Coating

Hydrogen charging conditions were chosen to deliver realistic hydrogen contents of up to 1 ppm:

1st level: no charging – expected hydrogen content of ≈ 0.05 ppm.

2nd level: charging in 0.5M H₂SO₄ with 0.2 g/l Thiourea for 45 or 90 minutes – expected hydrogen content ≈ 0.5 ppm. Two different charging times were used to provide different hydrogen contents but turned out to deliver the same hydrogen level, thus 45 minutes are considered sufficient for complete saturation of the material by the chosen charging solution.

3rd level: charging in 0.5M H₂SO₄ with 1.0 g/l Thiourea for 120 minutes – expected hydrogen content of ≈ 1.0 ppm.

Immediately after charging the samples were cleaned and electro-galvanized to lock the hydrogen in the material. The samples were then stored in liquid nitrogen.

4.3. Distribution

The samples were simultaneously distributed among the partners. To ensure cross-check of the labs, all samples were stamped (100 mm x 50 mm) and mixed directly before shipping. After arrival, all participants stored the samples in liquid nitrogen at the same time ensuring a similar hydrogen loss during transport. The total time without cooling was 72 hours.

4.4. Sample preparation before measurement inclusive simulation of effusion

The area affected by hydrogen effusion through the sheared edge during transport was estimated to be a distance of about 5 mm from the edge and therefore was removed. The remaining material was stamped into samples of about 20 mm x 45 mm, which were then either temporary stored in liquid nitrogen or directly processed: de-coated, cleaned and measured.

De-coating was performed in 20% HCl solution with 5 g/l Hexamethylenetetramine until the gas formation induced by Zn-dissolution stopped, followed by rinsing in a water bath and drying with compressed air. The duration of all preparation steps was recorded.

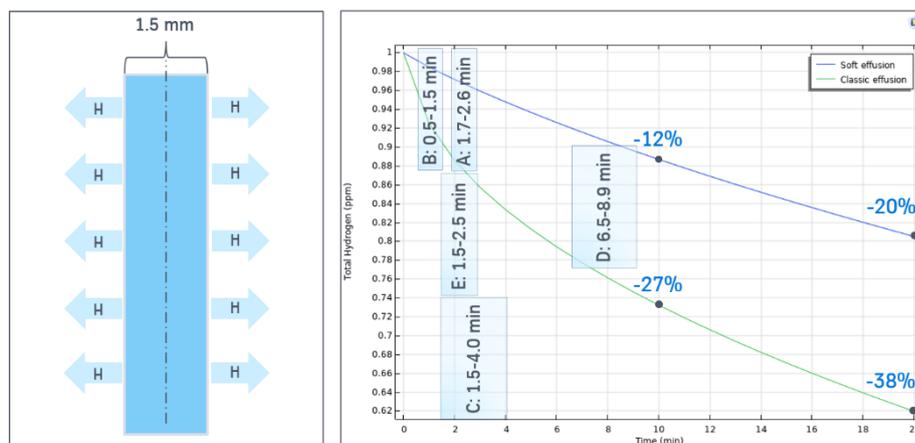


Figure 1: Hydrogen loss versus time after de-coating.

The most sensitive period in preparation is the time after removal of the coating and before the start of measurement. Within this period hydrogen effuses out of the entire surface area of the samples. The following figure shows the simulated hydrogen content for a sample with 1 ppm as a function of effusion time after de-coating. After 10 minutes a sample loses 12 to 27% of the initial hydrogen content. The “classic effusion” curve corresponds to boundary conditions where the hydrogen content on the surface is zero, meaning that the whole hydrogen escapes out of the sample immediately after arrival at the

surface. The “soft effusion” curve represents a case, where an energetic barrier hinders hydrogen from leaving the sample. Both curves show extreme cases and the real curve lays somewhere in between depending on many factors like surface condition, material, surrounding media, etc.

All labs used their best practices to reduce the time between de-coating and measurement. Lab D was able to reduce this time to 0.5 to 4 minutes, during which time no significant strong deviations are expected.

4.5. Measurement

Table 1 summarizes equipment used in the present round-robin-test. Each lab performed 2 isothermal and 2 heat ramp measurements on each half-sample. The remaining 5th sample was used for different additional measurements. Lab A stored the 5th samples for analysis of the long-term storage in liquid nitrogen. Lab B performed additional isothermal measurements. Lab D performed additional heat ramp measurements. Lab E applied their internal standard procedure for storing the samples in liquid nitrogen after de-coating.

Table 1: used devices for hydrogen determination

Lab	Equipment	Calibration	Typical sample size and weight [mm x mm] --> [g]
A	LECO DH603 (isothermal measurements)	Standard reference material (every second day)	100 x 20 mm ² --> 20-40 g
	Bruker G8 Galileo (constant heating rate)	N ₂ +H ₂ gas / Standard reference material	100 x 20 mm ² --> 20-40 g
B	Bruker G4 Phoenix wit TCD	N ₂ +H ₂ gas (1x per day when measuring)	50 x 15 mm ² --> 5-40 g
C	Bruker G8 Galileo + IR07	H ₂ gas bottle (1x per day)	120 x 25 mm ² --> 15-60 g
D	Homemade TDA detection with mass spectrometer	N ₂ +H ₂ gas bottle (50ppm) (1x per day)	50 x 20 mm ² --> 10-20 g
E	Bruker G8 Galileo + IR07 + PI ESD100	N ₂ +H ₂ gas (1x per week or when measuring)	50 x 20 mm ² --> 10-20 g

Isothermal measurements were performed at a temperature of 300°C for 800 seconds with heating under typical lab conditions. Ramp-measurements were performed at a constant heating rate of 1 K/s up to a temperature of 600°C.

5. Results

5.1 Isothermal measurement

Table 2 summarizes average values and standard deviations for the isothermal measurements. The deviations within single samples were generally very small. The majority were below $\pm 0,05$ ppm. Average deviations over the same charging level were slightly higher but still mostly below $\pm 0,05$ ppm. These observations reflect the chosen sample preparation methodology used by the labs.

Since the hydrogen effusion depends on the initial hydrogen content and is expected to be negligibly small for the reference material within the investigated timeframe, identical results are expected for this case. Nevertheless, Labs A and B measured contents of 0.21 to 0.26 ppms, which are about 0.15 ppm higher than the values measured by other labs or than the numerically predicted value. Labs A and B are also the only ones that detected a second peak in isothermal curves. This discrepancy might be caused by a residual Zn layer or by remaining electrolyte on the surface. This demonstrates the importance of de-coating until the gas formation completely stops and of thoroughly cleaning the samples to avoid distortion of the results.

The temperature curves shown in figure 2 indicate that the main part of hydrogen effuses during heating up to the isothermal state.

Furthermore the figure shows that the chosen measurement duration was sufficient. This is indicated by the hydrogen signal measured by all labs, which returning to the base line within 600s, even though the temperature of 300°C was not reached in some cases. Additionally, it made no difference whether the temperature was measured by thermocouples welded directly on the sample surface or by measurement of the furnace chamber.

According to the average hydrogen contents measured for the same charging levels the labs can be clustered in three groups: (A, B) > (E) > (C, D).

Table 2: Average hydrogen content and standard deviation [ppm] for isothermal measurements at 300°C

Reference	Lab A	Lab B	Lab C	Lab D	Lab E
Sample 25	0,21 ± 0,04	0,26 ± 0,01			
Sample 26			0,10 ± 0,01		
Sample 27				0,11 ± 0,01	0,10 ± 0,01
Average	0,21 ± 0,04	0,26 ± 0,01	0,10 ± 0,01	0,11 ± 0,01	0,10 ± 0,01

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0.2 Thio - 45 Min	Lab A	Lab B	Lab C	Lab D	Lab E
Sample 5	0,68 ± 0,11	0,61 ± 0,05			
Sample 6		0,62 ± 0,10			
Sample 7			0,32		
Sample 8			0,32 ± 0,02	0,38 ± 0,00	
Sample 9				0,36 ± 0,01	0,54 ± 0,00
Sample 10	0,66 ± 0,01				0,49 ± 0,02
Sample 11	0,65 ± 0,05		0,27 ± 0,07		
Sample 12		0,72 ± 0,07		0,40 ± 0,01	
Sample 13					0,46 ± 0,00
Average	0,66 ± 0,05	0,66 ± 0,08	0,30 ± 0,05	0,38 ± 0,02	0,50 ± 0,04

0.2 Thio - 90 Min	Lab A	Lab B	Lab C	Lab D	Lab E
Sample 15	0,67 ± 0,12				
Sample 16		0,58 ± 0,08	0,29 ± 0,02		
Sample 17				0,36 ± 0,01	
Sample 18			0,28 ± 0,03		0,57 ± 0,08
Sample 19	0,68 ± 0,01			0,33 ± 0,03	
Sample 20		0,53 ± 0,08			0,49 ± 0,01
Sample 21	0,68 ± 0,06			0,33 ± 0,01	
Sample 22		0,48 ± 0,05			0,40 ± 0,00
Average	0,67 ± 0,06	0,53 ± 0,07	0,28 ± 0,02	0,34 ± 0,02	0,52 ± 0,05

1.0 Thio - 120 Min	Lab A	Lab B	Lab C	Lab D	Lab E
Sample 1					0,92 ± 0,01
Sample 2	1,29 ± 0,01		0,86 ± 0,11		
Sample 3		0,97 ± 0,07		0,62 ± 0,01	
Sample 4			0,65 ± 0,06		
Average	1,29 ± 0,01	0,97 ± 0,07	0,76 ± 0,14	0,62 ± 0,01	0,92 ± 0,01

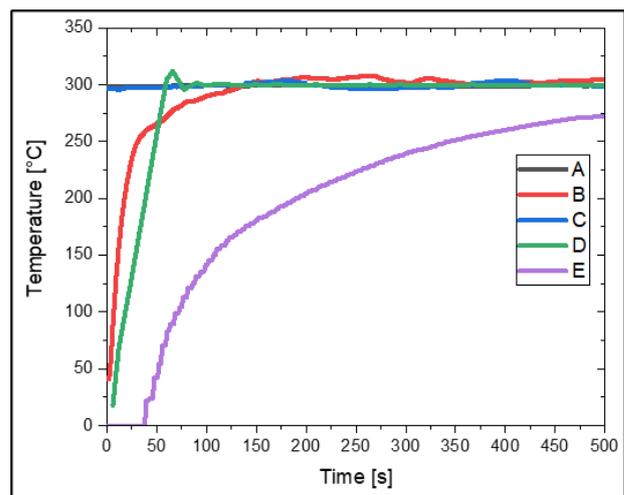
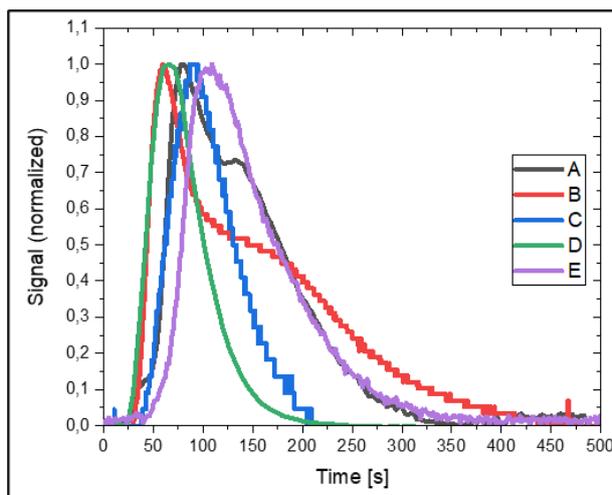


Figure 2: Example of isothermal curves for the reference material (no charging).

5.2 Heat ramp

Average hydrogen contents measured using the heat ramp are summarized in the following table. Unfortunately, de-coating in Lab B was performed in a different manner, thus the corresponding results are not included in the comparison.

In contrast to the previous isothermal results, Lab A performed heat ramp analysis with a Bruker G8 device and the results are in a better agreement with Labs C, D and E. Due to the lower heating rate comparing to isothermal mode the measured signal [ppm/sec] is also lower, leading to slightly underestimated values and higher standard deviations. This effect becomes more pronounced with decreasing heating rate. Therefore, it is recommended to maintain the heating rate at a high level to avoid deviations due to limits of detection and to keep the measurement time acceptably short.

Besides the results of the Lab C, all labs delivered comparable results for the second hydrogen level. Due to the longer preparation times, Lab D measured lower values compared to others.

Table 3: Average hydrogen content and standard deviation [ppm] for measurements at a heating rate of 1 K/s

Reference	Lab A	Lab B	Lab C	Lab D	Lab E
Sample 25	0,14 ± 0,01				
Sample 26			0,09 ± 0,01		
Sample 27				0,11 ± 0,00	0,07 ± 0,00
Average	0,14 ± 0,01		0,09 ± 0,01	0,11 ± 0,00	0,07 ± 0,00

0.2 Thio - 45 Min	Lab A	Lab B	Lab C	Lab D	Lab E
Sample 5	0,46 ± 0,04				
Sample 6					
Sample 7			0,27 ± 0,01		
Sample 8			0,25 ± 0,04	0,39 ± 0,05	
Sample 9				0,39 ± 0,01	0,46 ± 0,01
Sample 10	0,46 ± 0,02				0,35 ± 0,04
Sample 11	0,38 ± 0,07		0,25 ± 0,03		
Sample 12				0,37 ± 0,03	
Sample 13					0,47 ± 0,01
Average	0,43 ± 0,05		0,25 ± 0,02	0,38 ± 0,03	0,43 ± 0,06

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0.2 Thio - 90 Min	Lab A	Lab B	Lab C	Lab D	Lab E
Sample 15	0,42 ± 0,06				
Sample 16			0,24 ± 0,03		
Sample 17				0,37 ± 0,09	
Sample 18			0,26 ± 0,01		0,44 ± 0,06
Sample 19	0,39 ± 0,02			0,34 ± 0,01	
Sample 20					0,29 ± 0,02
Sample 21	0,44 ± 0,02			0,36 ± 0,02	
Sample 22					0,34 ± 0,08
Average	0,41 ± 0,04		0,25 ± 0,02	0,36 ± 0,05	0,35 ± 0,08

1.0 Thio - 120 Min	Lab A	Lab B	Lab C	Lab D	Lab E
Sample 1					0,82 ± 0,05
Sample 2	1,01 ± 0,06		1,03 ± 0,1		
Sample 3				0,73 ± 0,07	
Sample 4			0,59 ± 0,04		
Average	1,01 ± 0,06		0,81 ± 0,26	0,73 ± 0,07	0,82 ± 0,05

Example heat ramp curves in the following figure show that even under identical conditions (sample geometry, hydrogen content, heating profiles etc.) the position of peaks are far from being the same. Considering this observation, the widely-used Kissinger analysis of the energies would be unsuitable especially if results are compared to those measured by other labs using different equipment.

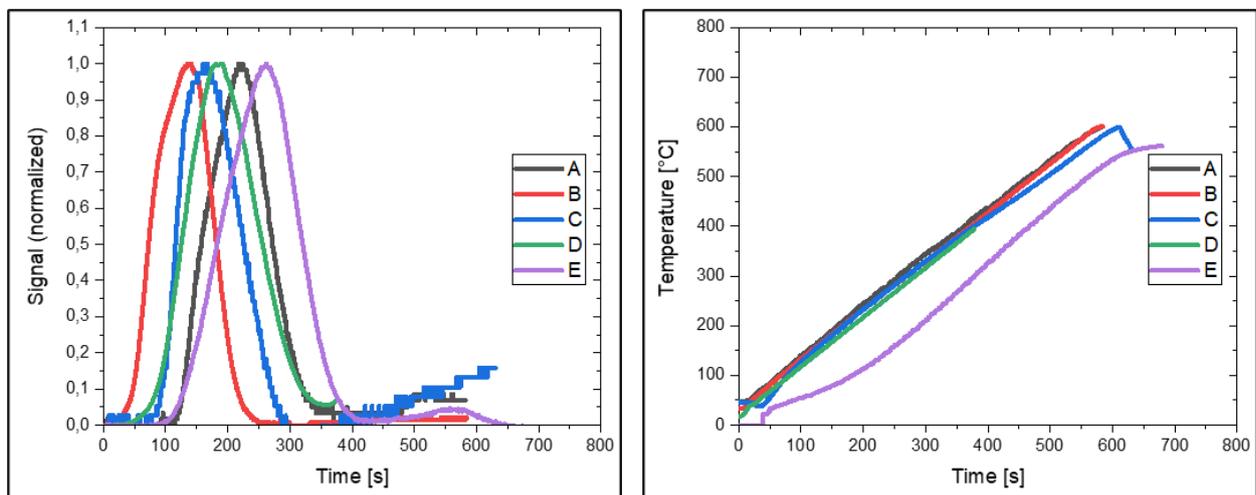


Figure 3: Example curves for the intermediate material (charging with 0.2 Thio for 90 Min).

5.3 Optimization of de-coating

Considering previous observations that de-coating time can strongly affect the measured hydrogen content an additional study was performed in which different de-coating solutions were tested on the

remaining samples without hydrogen charging. De-gassed material without hydrogen charging prior to zinc coating results in the lowest possible hydrogen content. Higher values indicate hydrogen uptake during de-coating.

As expected, de-coating in undiluted HCl solution requires less time and therefore is a preferred method, limiting the time for hydrogen effusion or uptake. Measurements without the use of an inhibitor (not shown) caused significantly higher values (+0.20...0.25 ppm) and resulted in strong gas formation, which led to splashing of the de-coating solution. Due to high hydrogen uptake and for safety reasons, de-coating without an inhibitor is not recommended. With inhibitor concentrations of 5 g/l and higher the measured hydrogen content was unchanged. Considering these results, de-coating in undiluted HCl with 5 g/l Hexamethylenetetramine (37% HCl + 5 g/L THM) is recommended.

Table 4: Results of de-coating optimisation.

Lab	Sample	Decoating solution	Decoating time [s]	H-Content [ppm]	
B	28-1	20% HCl + 5 g/L THM	48	0,15	0,14 ± 0,02
	28-2	20% HCl + 10 g/L THM	49	0,15	
	28-3	20% HCl + 20 g/L THM	45	0,11	
	28-4	37% HCl + 5 g/L THM	50	0,10	0,11 ± 0,01
	28-5	37% HCl + 10 g/L THM	46	0,12	
	28-6	37% HCl + 20 g/L THM	52	0,12	
E	28-1	20% HCl + 5 g/L THM	96	0,20	0,19 ± 0,03
	28-2	20% HCl + 10 g/L THM	106	0,22	
	28-3	20% HCl + 20 g/L THM	108	0,16	
	28-4	37% HCl + 5 g/L THM	43	0,08	0,08 ± 0,01
	28-5	37% HCl + 10 g/L THM	50	0,08	
	28-6	37% HCl + 20 g/L THM	50	0,07	

5.4 Storing in liquid nitrogen

As mentioned before, Lab E stored one sample in liquid nitrogen directly after de-coating. After the storing for two to three weeks the samples were cleaned and at the same time heated up to the room temperature in an acetone bath, dried with compressed air and measured. The total additional preparation time was around 100 s. The results are summarized in the following table. According to these results, storing of de-coated samples in liquid nitrogen lowered the measured hydrogen content and thus should be avoided if possible.

Table 5: Comparison of the direct measurement vs. storing in liquid nitrogen.

Material	Directly measured [ppm]	Stored in liquid N ₂ [ppm]	Difference [ppm]
Reference	0,10 ± 0,01	0,13	+ 0,03
0.2 Thio - 45 Min	0,50 ± 0,04	0,44 ± 0,04	- 0,06
0.2 Thio - 90 Min	0,52 ± 0,05	0,39 ± 0,05	- 0,13
1.0 Thio - 120 Min	0,92 ± 0,01	0,88	- 0,04

The Influence of a long-term storage in liquid nitrogen was investigated by Lab A. After storing for over 9 months in the initial state (as delivered / Zn-coated) the samples were prepared and measured according to the standard procedure. The results are summarized in the following table. According to the results, storing of Zn-coated samples in liquid nitrogen increased the measured hydrogen content and thus should be avoided as well. If a long-term storage is necessary, it should be limited to several month and performed in the coated state to minimize hydrogen loss.

Table 6: Comparison of the direct measurement vs. long term storing in liquid nitrogen.

Material	Directly measured [ppm]	Stored in liquid N ₂ [ppm]	Difference [ppm]
Reference	0,14 ± 0,01	0,21	+ 0,06
0.2 Thio - 45 Min	0,43 ± 0,05	0,52 ± 0,03	+ 0,09
0.2 Thio - 90 Min	0,41 ± 0,04	0,52 ± 0,03	+ 0,11
1.0 Thio - 120 Min	1,01 ± 0,06	1,25	+ 0,24

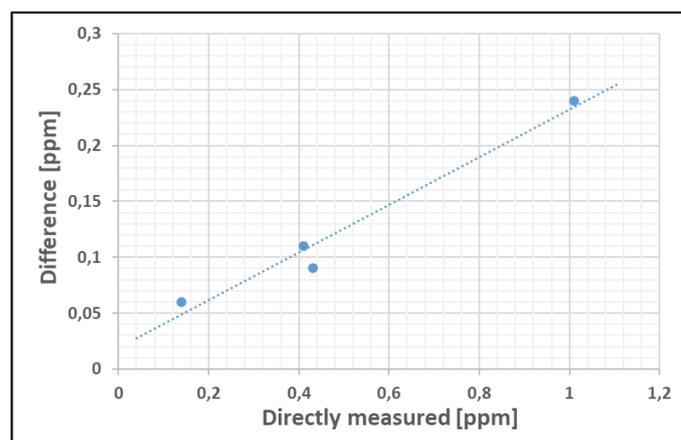


Figure 4: Hydrogen uptake after a long-term storing in liquid nitrogen.

An interesting observation arises from the following figure. It shows that hydrogen uptake during the long-term storage is related to the charged content and therefore should come from the charging procedure and not from the material or coating. One possible explanation could be a thin hydrogen-rich

layer adsorbed on the plate surface, which has enough time to absorb into material after coating. Further investigations are needed to better understand this phenomenon.

5.5 Summary of results

Parallel measurements on the same sample by different labs show very low standard deviations. This leads to the conclusion that the most deviations in this round-robin-test resulted from sample preparation and measurement procedures and not from prior treatment (charging and coating).

To reduce deviations, the time between de-coating and start of the measurement must be kept as short as possible; the longer the duration the less the detected hydrogen. Another important factor is hydrogen uptake during de-coating, which can be reduced by de-coating in an undiluted HCl solution with 5 g/l Hexamethylenetetramine acting as inhibitor.

Extended storage of de-coated samples in liquid nitrogen reduces hydrogen content and should, therefore, be avoided if possible. Long term storage of zinc coated samples in liquid nitrogen might lead to higher hydrogen contents due to surface and zinc-coating effects and should be considered only if necessary.

Analysis of the binding energies using Kissinger approach does not deliver comparable results and should be avoided or limited to comparison within one lab.

6. Summary of derived recommendations

- Storage in liquid nitrogen
 - Thawing with running cold water or in an acetone bath within 30s + 10s cleaning with compressed air.
 - Limited to a maximum of 3 months in total in Zn-coated condition.
 - Measurement after sample removal preferred.
- Sample preparation
 - Time span must be kept as short as possible yet consistent for every test and should be documented for comparison.
 - Recommended de-coating solution: 37% HCl + 5 g/L Hexamethylenetetramine.
- Isothermal measurement at 300°C (or 350°C)
 - Controlling the furnace temperature is sufficient.
 - Applying thermo couples to sample surface not mandatory.
 - Duration: 800s for cold rolled material <3,0mm proposed for initial tests.

- A complete determination of weakly trapped hydrogen (diffusible hydrogen) requires the return to the baseline.
- Reduction of 800s possible if initial measurements show a faster return to the base line.
- Heat ramp measurements (recommendations for determination of weakly trapped (“diffusible”) hydrogen content only! Not appropriate for investigations of trap energies at higher temperatures due to limited signal integration up to 300-350°C etc.)
 - Heating rate between 0,1 and 1,0K/s (1,0 K/s in some cases close to maximum possible oven performance)
 - Higher heating rates recommended due to a shorter measurement time leads to less scattering.

7. (Dissemination)

Presented at VDA-working group for hot stamping materials in July 2021

A short summary presented at VDA “AK Feinblech” in November 2021