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Determination of diffusible and total hydrogen concentration in coated and uncoated steel using melt and solid extraction techniques: Part I

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ABSTRACT

It is essentially to know the bulk hydrogen concentration in various types of steel because it indicates the amount of hydrogen that can be trapped by the different alloys of steel. This information leads to more knowledge about the interactions of steel alloys with hydrogen containing environment and stability of the steel material during usage. To get this information precise analytical methods are necessary.

Although the analytical methods for the determination of hydrogen in steel samples are often discussed, there are no sufficient systematic studies as far as the influence of the sample preparation on the analytical value is concerned.

The influence of different sample preparation methods on the hydrogen determination in steel at parts per million levels by melting extracting methods has been investigated in this work. The hydrogen was measured by thermal conductivity and infrared detection. The flat sheet samples were zinc coated and uncoated ferritic types of steel. The zinc coating was removed by chemical (acid etching) and physical (paper scraping) methods. Dichloromethane acetone/ethanol, tetrachloromethane and alkaline steel cleaner (Ridoline C72) have been used for cleaning the surface of uncoated samples. The results of the total hydrogen content obtained by applying the different methods were evaluated.

1. Introduction

Steel production process is highly susceptible to hydrogen contamination during steelmaking, fabrication and service [1]. The more hydrogen amounts present in steel products, the more the risk of hydrogen embrittlement which causes the quality deterioration resulting into short lifespan of the material.

The hydrogen interacts with steel by adsorption on external steel surfaces and absorption into the internal crystal structure resulting in hydrogen embrittlement [2]. The hydrogen is transported by diffusion and localization into the internal sites of the bulk metal [1,3].

The processes that enhance hydrogen influence on steel involve the exposure of the steel to air moisture during welding, forging and casting. The galvanic metal deposition, cathodic corrosion protection and pickling processes encourage hydrogen entrance because they release atomic hydrogen that affects the steel. The presence of high temperature and pressure highly contribute to the embrittlement of steel by hydrogen.

The mechanism of hydrogen interactions with steel involves the adsorption of the molecular hydrogen from the gaseous phase onto the metal surface. When steel is exposed to acidic conditions hydrogen can enter the steel due to electrochemical reactions. The following reactions occur by treating steel with 6% (w/w) H_2SO_4 and 0.05% (w/w) As_2O_3 as a promoter for hydrogen adsorption at a current of 0.62 mA.

The atoms are also adsorbed on the metal surface and loose the electrons to become protons by interacting with the crystal lattice electrons. Protons have a much smaller radius that permits them to diffuse fast and easily throughout the metallic crystal structure. The hydrogen protons occupy the interstitial sites in the metallic structure. Due to the pressure exerted by the presence of hydrogen protons the structure becomes hard and brittle. But some of the atoms remain adsorbed on the metal surface and can recombine to form hydrogen molecule which is desorbed out of the metal as gas. This occurs when the partial pressure in the metal is exceeded by the atmospheric pressure.

The hydrogen protons that are in the inner crystal lattice regain the electron from the metal lattice electrons. This atom from the inner crystal structure recombines with the adsorbed atom on the metal surface and they are released out of the metal [4–7] (Fig. 1).

Therefore, hydrogen interactions with steel, e.g. diffusion into the metal, occupation of the interstitial sites between the crys-

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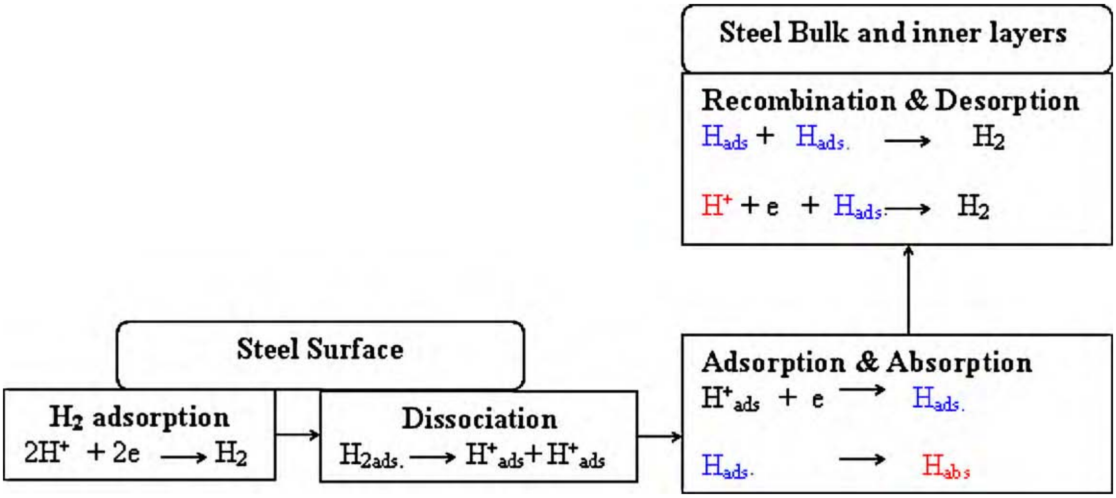

Fig. 1. Diagram of interactions of hydrogen with steel.

tal lattice particles and desorption are destructive to the steel products. They cause fissures and pores in the inner structure which result in microcracks. Then the affected material may have a decrease in strength and ductility and become unreliable for the purposes or services.

Melt extraction methods have been applied for the analysis of total hydrogen concentration in steel materials [8–10]. The sample is heated in the impulse furnace consisting of direct current electrodes that heat the graphite crucible by resistance up to a temperature of 3000 °C. The released gases like hydrogen, oxygen and nitrogen are led into the thermal conductive detector or infrared detector [11,12]. Presently the steel industries coat their samples with zinc, to extend the lifespan of the steel products. Zinc will be used for this purpose because of lower costs. Normally, the total hydrogen content is measured in uncoated and etched samples to monitor the quality of that particular product. However, the coat removal method and the sample cleaning method may cause the hydrogen to diffuse out or into the sample. This work demonstrates the dependence of hydrogen concentration on sample preparation according to Fig. 2.

Following the theory the hydrogen concentration is expected to be higher at the middle layer due to oxides dominating the interface [13]. The investigations have been focussed on total and diffusible hydrogen determination in steel [14]. Most analysts deal with the determination of hydrogen concentration absorbed or adsorbed in steel based alloys, hydrogen trapping characteristics, the influence of sample storage conditions on hydrogen concentration in steel and the amount of hydrogen entering the steel during electrolytic charging hydrogen [13–15]. The hydrogen analysis in zinc coated samples is mostly performed by removing the Zn coating chemically without properly control if the zinc coat is completely removed [8]. The influence of the surface structure and composition on hydrogen amounts is not properly investigated. The total hydrogen concentration in steel can be influenced by external conditions. The storage conditions of the samples, e.g. at room temperature may cause the diffusion of the hydrogen out of the steel. Also the sample cooling methods, e.g. with water or liquid N_2 can make a variation in hydrogen concentration of the same alloyed sample. Finally, the surface treatment/preparation before hydrogen analysis may increase or decrease the hydrogen content in steel. At least the analysis of differently prepared sample surfaces provides information about hydrogen location and behaviour in coated steel. It also gives the information about the ability of the coating to withstand hydrogen. For quantification of total hydrogen concentration, two carrier gas techniques that measured hydrogen by thermal conductive detector and infrared detection were compared. Both methods use electrode furnace and pyrocoated graphite crucibles to melt the sample while the analyte was carried by a gas to the detector. The time of the whole analysis is about 2 min. But there are challenges that face carrier gas systems with an electrode furnace that uses N_2 in the presence of graphite crucibles [12,16]. The use of nitrogen as the analyte carrier gas at high temperatures that are approximately 3000 °C causes violent reaction of nitrogen (carrier gas) with hydrogen from the sample to form ammonia (NH_4) and the carbon from the graphite crucible can react with hydrogen and nitrogen to result in hydrogen cyanide (HCN).

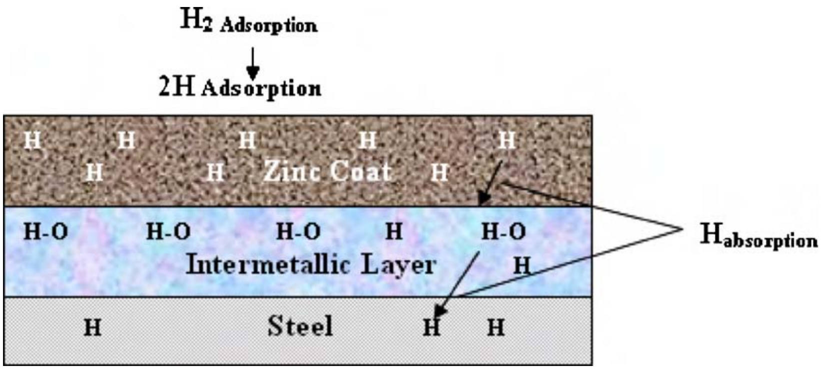

Fig. 2. Cross-section of zinc coated steel flat sheet.

Therefore these techniques require high temperature and time control during sample melting and hydrogen extraction from metallic materials, e.g. heating the sample at approx 2200 °C within an optimum period allowed the sample to melt gently while the hydrogen was being desorbed. Both techniques employ an inner smaller crucible for holding the sample that is placed inside the outer bigger crucible which was placed between the electrodes to conduct electricity. The electrodes deposit electricity to the outer crucible for indirectly melting the sample inside the inner smaller crucible. Therefore, the heat is homogeneously distributed around the inner crucible for the extraction of gases from the melted sample. This prevents the direct reaction of the outer crucible with the melted sample which can lead to crucible corrosion and low recoveries of the analyte (hydrogen). Also the re-trapping of hydrogen on released carbon or other substances in the oven (getter effects) is prevented by using the inner crucible once and cleaning the oven quickly with a brush after three measurements.

The carrier gas melt extraction gas methods are very attractive in metallic industries for hydrogen analysis because they are easily designed for the task (practical), compact, rapid (fast) for routine analysis, less expensive and pressure within the system is easy to maintain unlike the complicated, huge instruments for vacuum extraction methods.

This study on sample preparation can also assist in studying the influence of coating characteristics on hydrogen concentration in steel. Future work will involve the determination of diffusible hydrogen in coated and uncoated steel samples. After investigations on the hydrogen concentration in the bulk of the sample, more information must be provided on the type of hydrogen bonding involved in steel whether it is easily diffusible at low temperatures of 50–350 °C or strongly bonded which requires higher temperatures of 1000–2200 °C. The diffusible hydrogen determination by hot/isothermal extraction (without melting the sample) compliments the bulk hydrogen analysis (melt extraction) by providing temperatures at which the hydrogen can be desorbed/released from the samples. This information can assist in improving the quality of steel. The work is still in process and this will be the content of a second paper.

This paper shows the effect of handling the steel surface differently on the hydrogen concentration in steel.

2. Experimental

2.1. Materials

Six different types of steel samples have been investigated. Two zinc coated samples (A, B) and one uncoated sample (E) with a thickness of 0.8 mm, two zinc coated samples (C, D) and one uncoated sample (F) with a thickness of 1.5 mm.

The characteristics of the steel mentioned above are described by Berns and Theisen [17]. All samples were cut to 5 mm × 5 mm blocks which were weighed to 1 g for each measurement. For the thinner samples (0.8 mm) 5 pieces were weighed together to 1 g. For the thicker samples (1.5 mm), 3 pieces were weighed together to 1 g.

2.2. Chemicals for zinc coat removal

(I) Coated samples (A, B, C, D) were etched with 16% (w/w) HCl in the presence of an inhibitor (5 g l^{-1} hexamethylenetetramine) of recombination reactions of hydrogen atoms out of the steel surface [18]. The samples were rinsed in 0.5% (w/w) sodium hydroxide solution and cleaned in dichloromethane in ultrasonic bath for 5 min.

(II) Another etching method was to employ a mixture of 65% (w/w) nitric acid, 100% acetic acid and 85% (w/w) ortho-phosphoric acid. Afterwards, the samples (A, B, C, D) were rinsed in distilled water three times and finally cleaned in methanol.

2.3. Mechanical procedure for removing zinc coat

(I) Silica carbide paper was used to remove the zinc coat. The samples were cut into stripes of 1 cm × 13 cm size. The zinc coating was scraped by a silica carbide paper and the stripes were cut into pieces of 5 mm × 5 mm size. Then they were cleaned with dichloromethane for 5 min in ultrasonic bath.

2.4. Cleaning procedure for uncoated samples

The uncoated samples were oiled to protect their contents from moisture induced staining during storage. The contaminations and oils on samples E and F surfaces were removed by different cleaning methods as follows:

(III) Dichloromethane for 5 min in ultrasonic bath, dry with air.
(IV) Rinsing the samples with acetone, ethanol and dry with nitrogen.
(V) Tetrachloromethane for 5 min and dry with air.
(VI) Ridoline C72 (alkaline cleaning solution), 5 min and dry with nitrogen.

2.5. Instrumentation for total hydrogen analysis

2.5.1. Hydrogen detection by thermal conductive detector

The instrument Eltra 2000 OHN measures the thermal conductivity (TC) of hydrogen at μg g^{-1} level. The measuring principle is shown in Fig. 3. It can alternatively operate as a simultaneous O_2/N_2 or as O_2/H_2 analyzer. Here the second alternative is described. The sample in the electrically heated graphite crucible is completely melted at approximately 2200 °C. Before the nitrogen carrier gas enters the furnace, it is cleaned with sodium hydroxide to remove carbon dioxide and with magnesium perchloride to remove any moisture within the gas. The dust particles are removed by cotton wool. The carbon from the graphite crucible reacts with the oxygen and produces carbon monoxide. The carbon monoxide is oxidised to carbon dioxide in the presence of a catalyst (Schütze reagent: iodinepentoxide (I_2O_5) on silica). The oxygen is measured as CO_2 by infrared detector. Afterwards CO_2 is absorbed by sodium hydroxide so that it would not be transported to the thermal conductive detector. The moisture formed during the gas transportation is removed by magnesium perchlorate. The hydrogen then is carried by pure nitrogen gas to the thermal conductive detector.

2.5.2. Hydrogen detection by infrared detector

The instrument Leco TCH600 uses the similar melting principle but the released hydrogen is converted to H_2O and is analyzed by infrared (IR) detection. After melting the sample at approximately 2200 °C, the gases like hydrogen, oxygen and nitrogen are released and carried by helium to CO and CO_2 sensitive IR cells. Then the copper oxide wire converts carbon monoxide (from oxygen and carbon in the graphite crucible) to carbon dioxide and hydrogen to H_2O. The gases pass through the following IR detectors for total hydrogen determination as H_2O [4]. The concentration of hydrogen is stoichiometrically calculated (Fig. 4).

2.6. Calibration

The calibration of both equipments is different. The Eltra OHN 2000 was calibrated by one point gas calibration. The gas entrance valve was adjusted to a fixed volume which was equivalent to 12.5 μg g^{-1} hydrogen. Because of its similar thermal conductivity to hydrogen, helium was used as calibration gas.

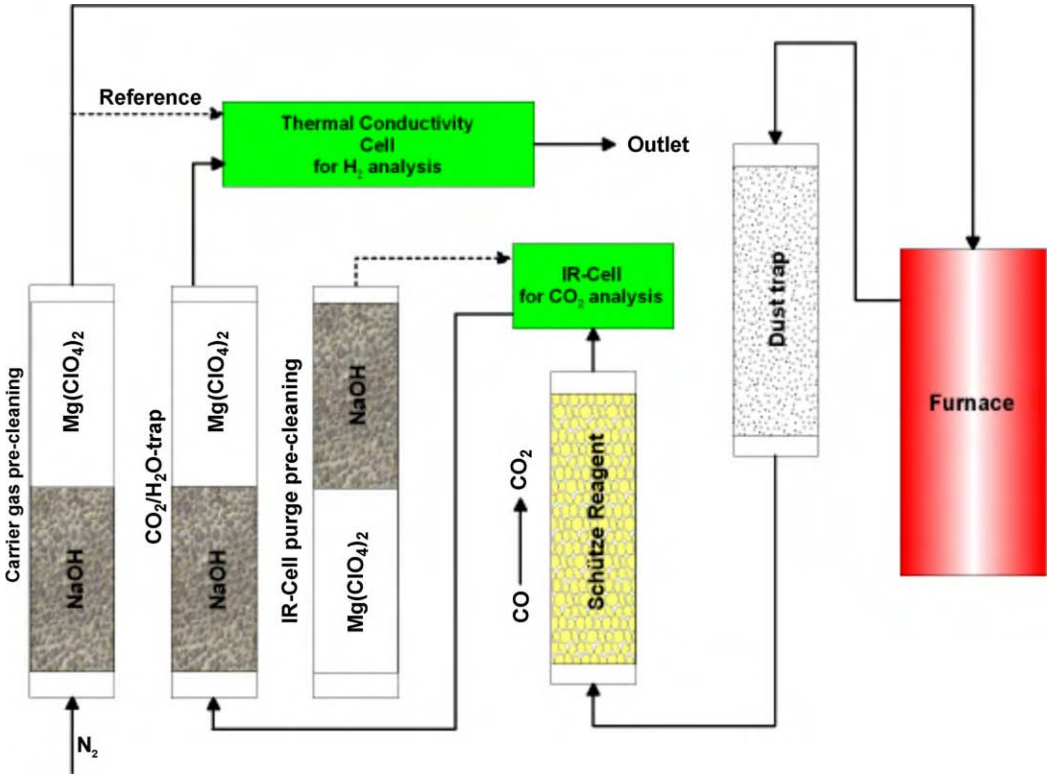

Fig. 3. Schematic diagram of Eltra OHN 2000 with TC detection.

To confirm the stability of the calibration, reference materials from Leco with certified hydrogen concentrations $c(H_2)_{747-762} = (1.8 \pm 0.4)\,\mu g\,g^{-1}$ and $c(H_2)_{501-529} = (6.0 \pm 0.2)\,\mu g\,g^{-1}$ were analyzed. The measured values were in agreement with the certified values as shown in Table 1.

For the calibration of Leco TCH 600 no gas calibration has been used but calibration with the same Leco reference materials. The results are shown in Table 1.

2.7. Additional equipment

The DSM 950 from Carl Zeiss Microimaging GmBH, Göttingen was used to observe the surface topography of the coated, filed and etched steel surfaces. The influence of the topography of the surface on the adsorption of impurities like hydroxides on it is probably. The rough surfaces are more susceptible to hydrogen or impurity adsorption than the smooth surface [19–21].

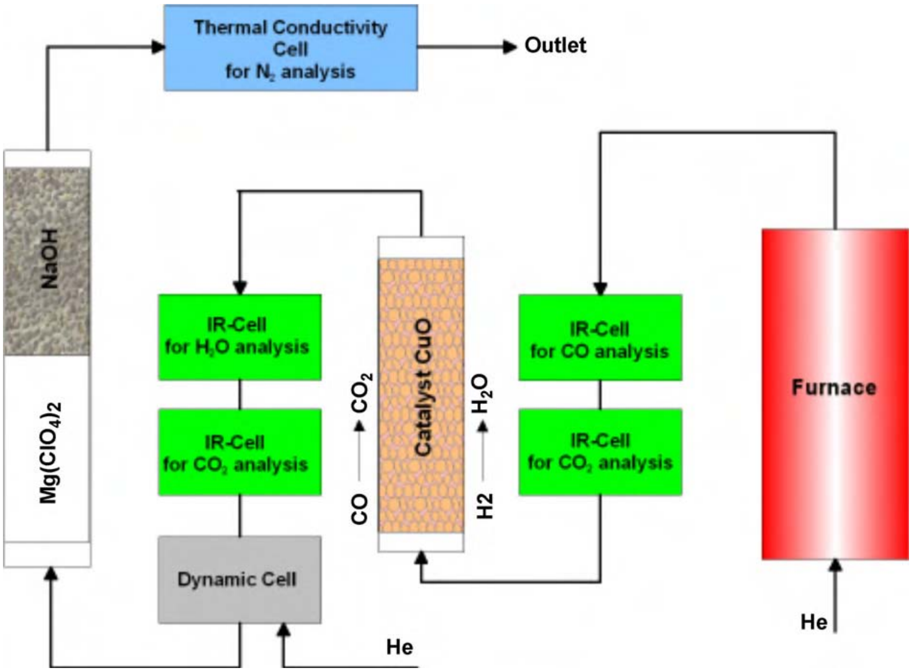

Fig. 4. Schematic diagram of Leco TCH 600 with IR detection.

Table 1
Calibration for the determination of hydrogen by thermal conductive (TC) and infrared (IR) detection at µg g^{-1}.

Detection method	Leco 501-5296.0 ± 0.2 µg g^{-1}	Leco 747-7621.8 ± 0.4 µg g^{-1}	He gas12.5 µg g^{-1}
Thermal Conductivity (TC)	5.88 ± 0.19	1.80 ± 0.12	12.42 ± 0.03
Infrared (IR)	5.91 ± 0.21	1.90 ± 0.14	
Number of measurements	10	10	10

Table 2
Hydrogen concentrations of samples A–D in µg g^{-1} measured by IR and TC detection.

Zn etching method	A	B	C	D
HCl (TCD)	0.83 ± 0.03	0.48 ± 0.03	0.93 ± 0.13	0.62 ± 0.12
NAP (TCD)	0.62 ± 0.10	0.31 ± 0.03		0.55 ± 0.11
HCl (IR)	1.17 ± 0.06	0.73 ± 0.07	0.85 ± 0.01	0.82 ± 0.10
NAP (IR)	0.94 ± 0.00	0.61 ± 0.03		0.68 ± 0.03

Table 3
Hydrogen concentrations in µg g^{-1} in coated, etched and scraped samples A and C.

Detection method	Sample	Coated	Etched	Scraped
TC	A	0.95 ± 0.11	0.83 ± 0.08	1.32 ± 0.02
	C	0.95 ± 0.04	0.85 ± 0.01	1.22 ± 0.09

The total amount of zinc in coated, filed and etched samples was determined by using ICP-AES from Thermo Fischer Scientific, Dreieich, Germany. The measurements were based on the determination of zinc concentration on different surfaces of the material. The investigations have been carried out in order to compare the variation of zinc concentration in zinc coated samples, acid etched samples and in paper scraped/filed samples. The zinc concentration was determined to observe if the zinc coating is totally removed so that the results will not be influenced by the hydrogen adsorbed on the zinc layer.

3. Results and discussion

3.1. Comparison of total hydrogen concentration in chemically etched samples

There was a slight difference in hydrogen concentration that has been obtained from HCl etching compared to NAP (nitric, acetic and phosphoritic acid) during thermal conductivity detection and infrared detection as indicated in Tables 2 and 3, Fig. 5a and b, respectively. As an example, during TC detection, the hydrogen concentration of sample B was calculated to 0.48 µg g^{-1} with HCl etching while a hydrogen content of 0.31 µg g^{-1} was obtained with nitric, acetic and phosphoric acid mixture by thermal conductivity hydrogen detection as shown in Fig. 5a. The hydrogen concentration of sample D was calculated to 0.62 µg g^{-1} with HCl etching while a hydrogen content of 0.55 µg g^{-1} was obtained with NAP etching. TC detection was applied as indicated in Fig. 5a. The presence of the inhibitor (hexamethylentetramine) during etching with HCl prevented the hydrogen from diffusing in or out of the steel during the zinc removal. It also inhibited the recombination reaction of the adsorbed hydrogen on the sample surface in acidic environment by forming a monolayer [22].

The application of NAP mixture indicated lower amounts of hydrogen. The adsorbed hydrogen atoms on the sample surface may have diffused out due to recombination reactions of the hydrogen atoms during etching. Hence lower concentrations of H_2 were obtained.

The same trend was observed by the results obtained from the analysis of the same samples by infrared detection. The hydrogen concentration determined by IR depends on the total conversion of H_2 to H_2O in the presence of copper oxide catalyst. Then, H_2O absorbed the radiation at a specific wavelength. Therefore, the accuracy of the measurement depends on the sample composition and the purity of copper oxide. These two factors can have minor influences on the results.

On the other side the accuracy of hydrogen analysis by applying thermal conductive detection depends strongly on the separation of H_2 from the carrier gas (N_2). The volume flow and the purity of the carrier gas have a big influence on complete separation of hydrogen. Therefore, less concentration of hydrogen can be measured by TC because of retention of a partial amount of hydrogen in the carrier gas.

Furthermore, it is possible that reaction of oxygen from the sample with carbon from the graphite crucible happens over the catalyst (iodine pentoxide). If the catalyst is less active oxygen reacts with hydrogen to form moisture (H_2O) which is removed by magnesium perchlorate before hydrogen analysis by TC detection. Hence low results can be obtained.

3.2. Comparison of total hydrogen in coated, etched and paper scraped samples

Although acid etching seemed to be a convenient method for removing the zinc coat, a physical method was applied to observe the difference in hydrogen concentration. The zinc coat was removed by scraping it off with a fine grain silica carbide paper.

The samples A and C were prepared by acid etching and scraping methods. The evolution of hydrogen was represented by different signals from differently prepared surfaces of the steel sample. The hydrogen concentration in the coated sample C was calculated to

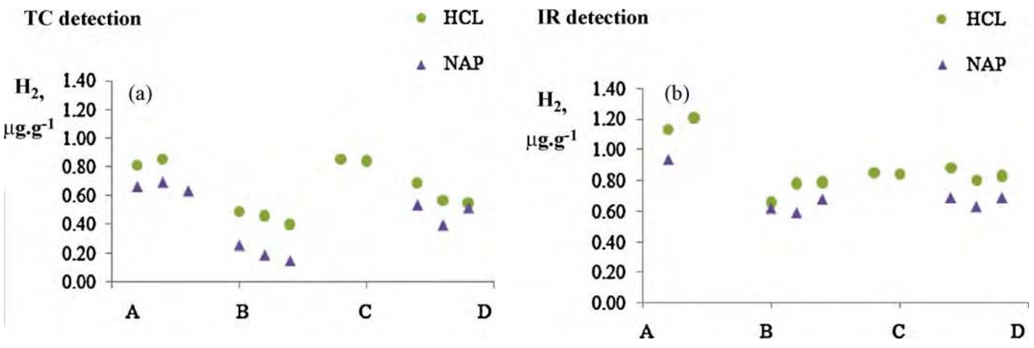

Fig. 5. Determination of total hydrogen concentration by thermal conductive detection and infrared detection at µg g^{-1} in A, B, C, D samples etched with HCl, NAP.

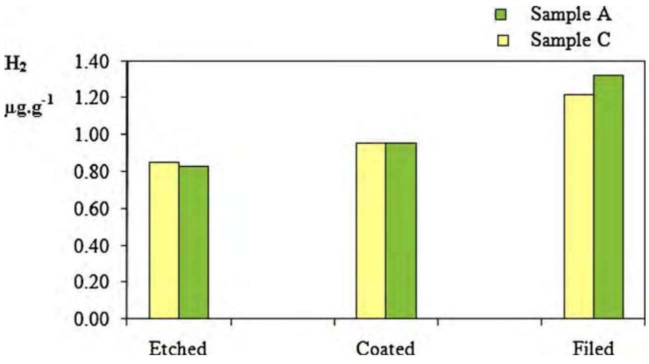

Fig. 6. Determination of hydrogen concentration (µg g^{-1}) in sample A and C measured by thermal conductive detection.

Table 4
Calibration for the determination of zinc by ICP-AES.

Analyte	Reference material	Certified values (µg ml^{-1})	Measured values (µg ml^{-1})
Zinc	B2-ZN02048	10.015 ± 0.020	9.98 ± 0.05
	D2-ZN02060	10077 ± 26	10044 ± 0.08
		1000000 ± 5000	1000000 ± 2700

0.95 µg g^{-1}, in the paper scraped sample to 1.22 µg g^{-1} and in the etched sample to 0.85 µg g^{-1} (see Fig. 6).

Variation in hydrogen concentration indicated amounts of hydrogen from the differently prepared sample surfaces, e.g. coated, paper scraped and etched samples. In each part of coated steel, the hydrogen was allocated in different amounts as shown in Fig. 6. It is highly possible that the high amount of hydrogen concentration in scraped sample was due to the contamination of the steel surface by silica carbide paper that introduced hydroxides.

The measurements with sample A type showed similar changes in hydrogen concentration like sample C as indicated in Fig. 6. The hydrogen content in the coated sample A was calculated to 0.95 µg g^{-1}, the content in etched sample to 0.83 µg g^{-1} and in paper scraped sample to 1.32 µg g^{-1}. This means that about 0.37 µg g^{-1} hydrogen was introduced into the sample through scraping.

Fig. 7 indicates the different surfaces of sample (D) that has been coated, scraped and etched. The coated sample was etched with 16% HCl to remove the layer. Then, the concentration of zinc in the solution was measured by ICP-AES. The paper scraped and etched samples were dissolved in aqua regia (HCl:HNO_3), ratio 2:1 and diluted in 25 ml aqua dest. The calibration has been carried out with Zn standard samples from Merck, Darmstadt, Germany listed in Table 4.

Table 5
Hydrogen concentration of sample A in µg g^{-1} measured by IR and TC detection.

Sample	Detection method	Coated	Etched	Paper scraped
A	Infrared	0.95 ± 0.11	0.83 ± 0.08	1.32 ± 0.02
A	Thermal conductivity	1.30 ± 0.07	1.17 ± 0.06	1.62 ± 0.21

The concentrations of Zn were calculated to $9.8 \times 10^5 \pm 0.12$ µg ml^{-1} in coated, $7.2 \times 10^3 \pm 0.11$ µg ml^{-1} in paper scraped and 1 ± 0.08 µg ml^{-1} in HCl etched samples. The hydrogen interacts with zinc in coated smooth surface samples to protect the steel. As the sample was scraped by silica carbide paper, the surface becomes rough and susceptible to the contamination by hydroxides which lead to more hydrogen recoveries. The surface conditions of the sample play a huge role during the analysis of hydrogen in steel samples because the interaction of hydrogen depends mostly on the surface area. The coated sample (Fig. 7a) has a smooth surface area which indicated that the hydrogen concentrations will mostly result from sample contents only. Unlike in Fig. 7b, where the sample was scraped with silica carbide paper to remove zinc and the process left a large rough surface area for more water adsorption, carbides and other contaminants. While the etched sample in Fig. 7c showed semi smooth surface which had less contaminants absorption ability due to the lower surface area.

The concentration of hydrogen in sample A was also measured by infrared detection. The hydrogen behaviour in the differently prepared samples was in similar pattern. The results obtained from measurements with infrared detection are shown in Table 5 together with results obtained from measurements with TC detection.

3.3. Comparison of different cleaning solvents

Four different cleaning solvents have been used to clean the surface of the uncoated samples (E, F). The methods are described in Section 2.

Dichloromethane was used as an organic cleaning agent for oil and oxides removal on steel. It is a polar solvent with a high volatility which makes it as an ideal solvent for removing grease and other contaminants from steel surfaces. Results obtained by TC detection measurements are shown in Fig. 8a and results obtained by IR measurements in Fig. 8b.

3.4. Detection of diffusible hydrogen amount by thermal desorption mass spectrometry

The damages in metallic materials are not caused by the amount of hydrogen absorbed but by the mobility of hydrogen in the material. Therefore, it is necessary to distinguish between diffusible and total hydrogen amount. The knowledge of the diffusible hydrogen amount provides information for a better evaluation of the susceptibility of the material towards hydrogen embrittlement.

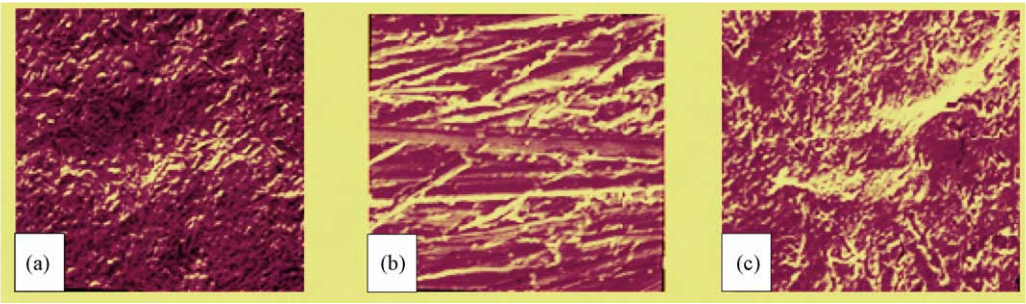

Fig. 7. Pictures of HCT sample made by DEM 950 (a) zinc coated surface, (b) scraped with fine grain paper (c) etched with 16% HCl. The spot of 10 µm was magnified to 1000×.

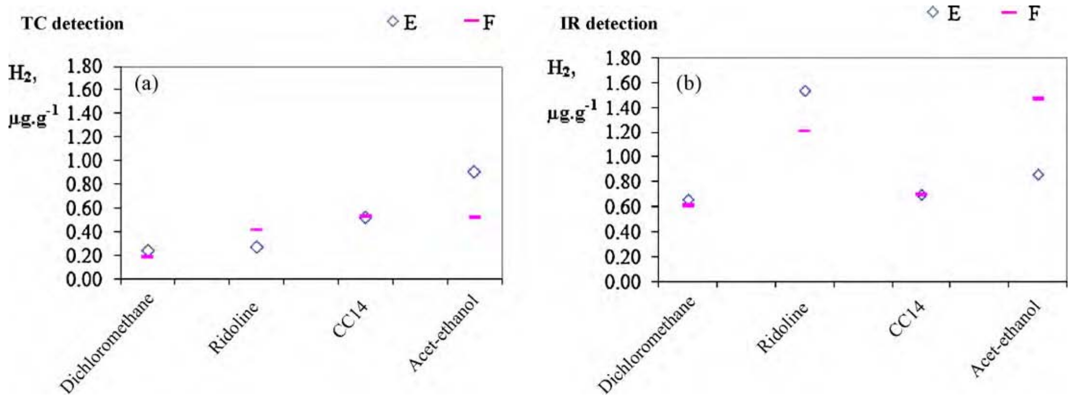

Fig. 8. Influence of the cleaning solvents on the hydrogen content in uncoated samples E and F by TC and IR detection.

A new quantitative and qualitative technique for the determination of diffusible hydrogen in metallic materials has been developed by coupling a carrier gas solid extraction analyzer with a compact quadrupole mass spectrometer to form a thermal desorption mass spectrometric technique (TDMS). First results of the ongoing research can be presented here but the complete work will be described in detail in a second paper.

The diffusible hydrogen in zinc coated (*D*) sample was measured by TDMS. The first peak of hydrogen was released at 250 °C containing 0.03 $\mu g\,g^{-1}$ hydrogen as shown in Fig. 9a. This diffusible hydrogen was adsorbed on the zinc sheet. Then, at 350 °C a broad peak occurred which indicated an incomplete separation hydrogen peaks due to strong hydrogen traps in the sample matrix that would have required higher temperatures to release well separated peaks. The Gaussian peaks were fitted to identify desorption temperatures and the diffusible hydrogen amount which was 0.3 $\mu g\,g^{-1}$ at a temperature between 350 and 690 °C.

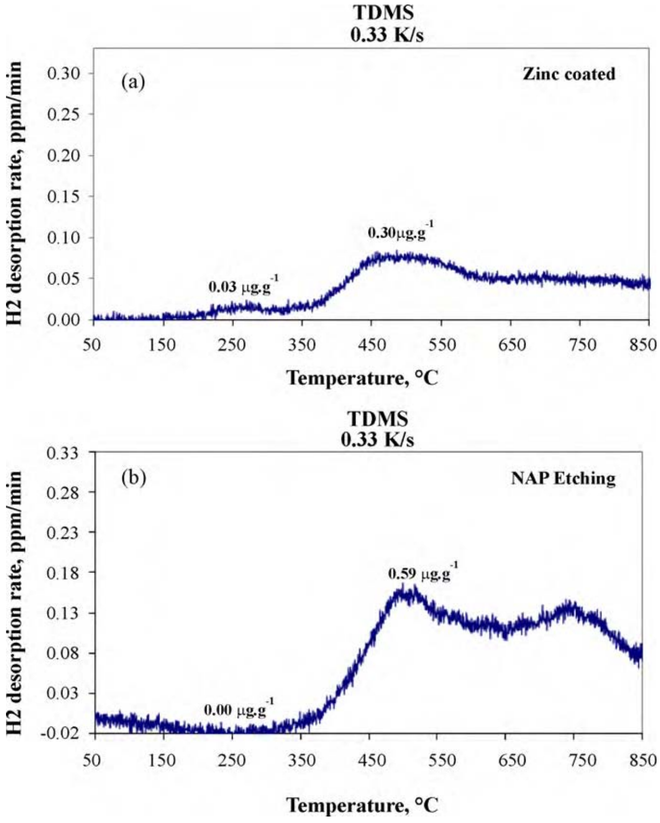

Fig. 9. Measurement of the diffusible hydrogen ($\mu g\,g^{-1}$) concentration in a (a) zinc coated sample by TDMS and (b) sample etched with NAP.

As the zinc coated sample was removed by etching with a mixture of nitric acid, acetic acid and phosphoric acid, there was no diffusible hydrogen at lower temperature between 100 and 380 °C as it is indicated in Fig. 9b. There was no diffusible hydrogen on the surface of the sample because it was released during zinc etching. The rest of the diffusible hydrogen (0.59 $\mu g\,g^{-1}$) was released later between 360 and 700 °C.

4. Conclusions

Based on the experiments performed, the sample preparation step is vital for the determination of hydrogen concentration in steel samples to be well informed about the characteristics of the product.

- When zinc coat was scraped off by a fine silica carbide paper, more contamination resulted in higher hydrogen concentration in the samples. Scraping left a rough surface which was highly susceptible to contaminations by oxides and hydroxides.

Therefore, the removal of zinc coat mechanically by scraping with a fine silica carbide paper is not recommended for hydrogen analyses in steel due to more sample contamination. It did not completely remove the interface layer covering the steel.

- Etching methods are the better alternative, whereas a slight difference between the two tested chemical solutions was observed. The application of nitric, acetic and phosphoric acid mixture indicated lower amounts of hydrogen than the application of hydrogen chloride acid for the etching process.
- The oils and oxides on the sample surface should be removed by an appropriate solvent. Dichloromethane was tested as the best cleaning solvent before hydrogen determination.
- The hydrogen concentrations obtained by the application of infrared detection confirmed the conclusions that were made concerning sample preparation and detection of the hydrogen concentration by thermal conductivity.

First results of the analysis of coated and uncoated steel samples by thermal desorption mass spectrometry confirm the already observed influence of the sample preparation on the detection of hydrogen amount and diffusible hydrogen amount, respectively. Further conclusions can be made after evaluation the ongoing experiments as far as the mobility of diffusible hydrogen concerned.

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