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Silva, Maria I.; Malitckii, Evgenii; Lehto, Pauli; Vilaça, Pedro

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Influence of sample extraction location on thermal desorption spectroscopy from a heat-resistant 13CrMo4-5 steel plate and correlation with microstructure features

Maria I. Silva^{*}, Evgenii Malitckii, Pauli Lehto, Pedro Vilaça

Department of Mechanical Engineering, School of Engineering, Aalto University, Espoo 02150, Finland

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ABSTRACT

Thermal desorption spectroscopy (TDS) is a highly sensitive and widely used method to directly measure the total hydrogen concentration and indirectly assess the hydrogen trapping sites and mechanisms from the spectra features in steels. Thus, there is a need to investigate the influence of sample location from a 5 mm plate of hot-rolled heat-resistant structural steel on TDS spectra. Via a new highly sensitive and specific correlation coefficient (*microToH*), the TDS results are correlated with low-angle grain boundaries volume fraction, grain size with different misorientation thresholds, microhardness, and geometrically necessary dislocations at different densities.

The results indicate that sample location influences 133 % and 62 % in the hydrogen desorption of peak 1 (at 515 K), and total hydrogen concentration via the influence of peak 2 (at 634 K), respectively. Thus, sample location needs to be considered as one relevant aspect in a research plan based on TDS analysis. The influence on peak 3 (at 762 K) was found to be negligible as it is related to the first exothermic peak of the heating cycle, associated with carbide precipitation phenomena. The individual grain analysis performed with high-resolution adaptive DMM and GND maps emphasises the accumulation of the deformation in the ferritic domain at the vicinity of the pearlite structures.

1. Introduction

In the scientific community, depending on the material and applications, hydrogen can be seen as desirable, for instance as an energy carrier; however, it is mostly unwanted in interaction with metals, where its uptake leads to hydrogen embrittlement, i.e. loss of a material's ductility due to hydrogen embrittlement effect [1,2,3]. Hydrogen uptake in metals can originate from the production process, welding, and from environmental exposure during service. In this work, we explore the highly sensitive hydrogen interaction with heat-resistant steel for exploration as hydrogen-as-a-probe in the inspection of material microstructure features and eventual detection of non-metallic inclusions and small-scale imperfections.

For a component's sample or replica, the concept of using hydrogenas-a-probe via thermal desorption spectroscopy (TDS) for inspection of the material condition is based on scanning the hydrogen desorption over temperature [4]. As different imperfections (or group of imperfections) will release the trapped hydrogen at different levels of activation energy, upon validation of the TDS results versus known microstructure features and discontinuities, the hydrogen-as-a-probe is an ultimately sensitive and high-resolution NDT technique for small-scale defects. Although the TDS of hydrogen is not a technique considered in the scope of NDT techniques, the very small size required for the samples to be extracted, e.g. 0.1 to 0.5 g for steel, enables measurement of hydrogen content in the vicinity of stress concentrators and in stress-affected zones without affecting the future performance of the engineering components. This technique takes advantage of the significant existing knowledge of the hydrogen-to-metal interaction. This phenomenon has been investigated since several decades ago, mostly on the scope of the hydrogen-to-metal interaction with respect to the hydrogen embrittlement problem, reporting about the role of hydrogen trapping and diffusion on hydrogen-induced fracture mechanisms [3,5,6,7,8]. A recent study on TDS revealed that there may be a correlation between hydrogen trapping and microstructure change caused by fatigue loading [9].

Hydrogen is known to be trapped by microstructure features and

* Corresponding author. E-mail address: maria.santossilva@aalto.fi (M.I. Silva).

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imperfections, namely: vacancies, substitutional atoms, dislocations, grain boundaries, phase interfaces, second phases, precipitates, microvoids and cracks [10,11]. The permeability, diffusivity and solubility of the hydrogen in steels are controlled by the temperature and microstructure of the studied material with a significant impact from chemical composition, crystal structure, microstructure features and defects [12, 13,14,15,16]. The TDS curves measured for austenitic stainless steel, ferritic stainless steel and ferritic-martensitic high-strength steel were found to have a certain relationship between microstructure and the mechanical property degradation caused by high hydrogen concentrations [17]. Zhou et al. [18], quantified creep damage (voids) in metallic alloys from the peak area of the TDS spectra. Another study revealed an influence of creep test conditions and microstructure changes with the TDS curve shape [19]. Escobar et al. [20], found a correlation between TDS peaks and specific microstructure features of different degrees of cold deformation in both transformation-induced plasticity (TRIP) steel and electrolytically pure iron. Besides TDS, there are few other techniques with microstructure sensitivity that can measure the content of hydrogen within a material, i.e. can quantify and correlate hydrogen content in bulk samples with certain microstructure features, like scanning kelvin probe [21,22], secondary ion mass spectroscopy [23, 24], atom probe tomography [25,26,27], or a combination of techniques [10,28]. The TDS has the distinct benefit of providing a rich information on the activation energy, associated with different hydrogen desorption phenomena.

One of the most common materials used in structural components of power plants is the heat-resistant special structural steel 13CrMo4–5 (EN 1.7335) [29,30,31], which is the focus of the present study. Although new modern ferritic/martensitic (F/M) steels are nowadays replacing the 13CrMo4–5 steel, in structural components of power plants, a large amount of power plants based on 13CrMo4–5 steel are still in service, including many in extended life period, where the evaluation of early damage is still of major importance. The typical origin of service time induced damage in power plant structural components is creep, creep-fatigue, environmental damage like corrosion, and neutron irradiation. Individually or combined, these mechanisms can compromise the performance and lifespan of the components [32,33,34].

This paper aims to understand the influence of the location of extraction of samples from a plate on the hydrogen TDS spectra and, therefore, on employing hydrogen-as-a-probe to characterise the material condition and detect eventual small-scale defects. The selected material to be investigated is a 5 mm hot-rolled heat-resistant special structural steel 13CrMo4–5 (EN 1.7335), in as-supplied condition. The TDS results are correlated with microstructure features assessed via differential scanning calorimetry (DSC), scanning electron microscopy (SEM), with energy dispersive X-ray analysis (EDX) and electron back-scatter diffraction (EBSD), and Vickers microhardness measurements.

The different locations of samples extracted from the 13CrMo4–5 steel plate are organised in three sets as shown in Fig. 1, namely:

 Set NtS – near-to-surface longitudinal cross-section (hereafter addressed as near-to-surface);



Fig. 1. Schematic view of TDS samples extraction plan from the studied 13CrMo4–5 steel plate: set NtS – samples extracted from near-to-surface lon-gitudinal cross-section (Near-to-surface); set M – samples extracted from middle longitudinal cross-section (Middle); set T – samples extracted from transversal cross-section TD/ND (Transversal).

- Set M middle longitudinal cross-section samples (hereafter addressed as middle);
- Set T transversal cross-section TD/ND samples (hereafter addressed as transversal).

Fig. 1 illustrates the normal direction (ND), rolling direction (RD) and transverse direction (TD) of the 13CrMo4–5 steel plate. ND corresponds to the thickness (t) of the plate.

2. Experimental conditions and methods

2.1. Material

Hydrogen trapping was studied for the heat-resistant low-alloy structural steel 13CrMo4–5 in as-supplied condition. The investigated 13CrMo4–5 steel was a plate of 5 mm in thickness. The chemical composition was measured upon receiving the material using an optical emission spectrometer (OES) ARL iSpark 8860. The chemical composition of the studied steel, according to standard EN10028–2, and measured by OES, is shown in Table 1.

2.2. TDS measurements

The 13CrMo4–5 steel samples for TDS analysis were extracted by high-precision machine cutting and were ground with 400/P800 grit SiC paper. After grinding, TDS samples were kept for 24 h in a desiccator at atmospheric pressure to provide the balanced hydrogen distribution within the sample bulk. Characteristic size of extracted samples is $2 \times 5 \times 15 \text{ mm}^3$ and characteristic final sample size for TDS measurements (i. e. after surface preparation) is $1.7 \times 4.5 \times 14 \text{ mm}^3$.

The TDS measurements were performed in temperature range from room temperature to 1073 K with the heating rate 10 K/min. To prepare for hydrogen partial pressure measurement in an ultra-high vacuum (UHV) chamber (at targeted pressure of 10^{-10} mbar), the sample was first placed in an airlock (AL) chamber, which was then pumped to an intermediate pressure of 10^{-5} mbar before being transported to the UHV chamber. The hydrogen partial pressure was measured in the UHV chamber with a SRS residual gas analyser RGA100 mass spectrometer. The temperature measurements were performed using a Type K thermocouple connected to the sample holder. After the measurements, the hydrogen partial pressure data was post-processed and the total hydrogen concentration from the spectra was calculated by removing the background measurement, corresponding to a TDS measurement without any sample, and by integrating the area below the desorption rate versus temperature curve.

The TDS spectra of this studied 13CrMo4–5, as it will be depicted later in §3.1, presents three well pronounced peaks and one broad peak in the background. The TDS curves were fitted with Gaussian peaks, as shown in Fig. 2, considering the peaks to correspond to a specific trapping site or to a group of the trapping sites of hydrogen in the studied steel. The background desorption peak was not analysed because it has no clear correlation to a trapping site or group of trapping sites as it occurs throughout the entire TDS measurement, so it could be originated from hydrogen adsorption/desorption at chamber components during the heating.

2.3. DSC measurements

Differential scanning calorimetry (DSC) measurements were performed using a NETZSCH STA 449F1 equipment. For this study, a heating rate of 10 K/min was used. The temperature and sensitivity calibrations were performed for 99.999 % samples of In (429.6 K), Sn (504.9 K), Bi (544.4 K), Al (933.3 K), Ag (1234.8 K) and Au (1337.2 K). 13CrMo4–5 steel sample with size of $\emptyset 2 \times 1.1 \text{ mm}^3$ and weight of 24.7 mg was used alongside two Al₂O₃ crucibles. The measurements were carried out under a protective Argon (99.9999 %) atmosphere. The

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Table 1

Chemical composition [wt.%] of the 13CrMo4-5 5 mm thick plate stee	el, according to standard EN10028–2 and measured by OES.
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[wt.%]	С	Si	Mn	Р	S	Cr	Мо	Ni	Cu	Al
EN10028–2 OES meas.	0.08 - 0.18 0.08	≤ 0.35 0.23	0.4 - 1 0.49	0.025 0.009	0.010 0.003	0.7 - 1.15 0.96	0.4 - 0.6 0.46	_ 0.05	0.3 0.03	_ 0.023
[wt.%]	W	v	Ti	Со	Nb	В	Pb	Sn	As	Fe



Fig. 2. Example of fitted TDS curve of as-supplied 13CrMo4-5 steel.

thermal cycles comprised the stages of heating at 10 K/min, holding at about 1423 K for 5 min, cooling at 10 K/min, and holding at about 373 K for 5 min. Before the DSC measurement, a correction test was performed to measure the response of the crucibles to the cycles and discard their effect in the test of the samples.

2.4. SEM, EDX and EBSD analysis

 $ND \equiv t$

t = 0 mm

Microstructure of the 13CrMo4-5 steel was studied using scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD) techniques. For the SEM, EDX and EBSD analysis, a Zeiss Ultra 55 field emission scanning electron microscope equipped with a Nordlys F+ camera, and with an HKL Nordlys Electron Backscatter Diffraction (EBSD) detector by Oxford Instruments were used, alongside the ZEISS SmartSEM software. The 13CrMo4-5 steel samples for microscopy and EBSD analysis were extracted by high-precision machine cutting, ground, mechanically polished, and finished to final condition with 0.02 µm colloidal silica vibratory polishing. The 13CrMo4-5 steel transversal cross-section TD/ND was studied by SEM after etching the surface of the specimen with tint etchant (10 % aqueous sodium metabisulfite) following the procedure proposed by Vander Voort [35]. As shown in Fig. 3, the SEM and EBSD analysis were performed for the transversal cross-section TD/ND, for near-to-surface (NtS), transition (Tr), and

Fig. 3. The location of the near-to-surface area (NtS), transition area (Tr), and middle area (M) within the steel plate transversal cross-section TD/ND. Properties for the whole transversal cross-section TD/ND = properties from 2 × near-to-surface area + 2 × transition area + middle area.

NtS

Tr

middle (M) areas, at a depth of t = 0 to 1 mm, t = 1 to 2 mm and t = 2 to 3 mm from the top surface, respectively. Assuming that the microstructure features of transversal cross-section TD/ND are symmetric, the microstructure properties characterising the whole transversal cross-section TD/ND area are estimated from considering the features obtained for "near-to-surface area + transition area + middle area + transition area + near-to-surface area", i.e. transversal cross-section TD/ND = $2 \times NtS + 2 \times Tr + M$. This assumption is supported by the quasi-symmetric results, presented later in §3.4, obtained from the microhardness (HV1) measurements of the whole transversal cross-section TD/ND area, considering the axis of symmetry located at mid-thickness (t = 2.5 mm).

The EBSD analyses were performed with a step size of 0.5 µm at a magnification of $2000 \times$ and grain boundary misorientation angle with threshold criteria of 5° Exception to these conditions are the individual grain analysis with high resolution adaptive domain median misorientation (DMM), and high resolution geometrically necessary dislocations (GND) density maps, where a step size of 0.1 µm at a magnification of $4000\times$, were used. The acceleration voltage used was 20 kV and the working distance was 20 mm. The indexing rate of the EBSD maps varied between 90 % and 92 % for 2000 \times magnification and between 91 % and 95 % for 4000×. The estimated angular measurement noise for the higher magnification is 0.23°, which was only calculated for the area Tr, which is the only result in higher magnification analysed in this study. The lower magnification estimated angular measurement noise is 0.33° for area NtS, 0.32° for area Tr, and 0.31° for area M. The calculations were performed according to [36], from 1st to 5th nearest neighbours, and the plots for average misorientation as a function of the kernel radius (first to fifth neighbours) are shown in Appendix A.

EBSD data processing was performed using MTEX toolbox [37,38], and software for EBSD measurement of deformation-induced dislocation sub-structures for MATLAB. The GND density calculations were done according to [37,38] and [39]. The grain size of the studied steel was calculated using the point-sampled intercept length method [40,41]. The grain boundary images were generated using EBSD data processed with MTEX as follows: 1) grain reconstruction procedure with threshold misorientation angles of 5° and 15°, and 2) removal of the grains with size less than 5 pixels. The grain sub-structures were analysed with the recently developed domain misorientation approach [42,43]. The EBSD maps were de-noised according to the parameters in Table 2 of [43], and the sub-structures were measured using misorientation thresholds $\Delta\theta=0.5^{\circ}$ and $\Delta\theta=2^{\circ}$, which are used to represent the dislocation cell and sub-grain structure, respectively [43]. The initial kernel size was set at

60 nearest neighbours.

2.5. Microhardness measurements

Microhardness measurements were carried out with a Duramin-40 tester according to EN ISO 6507 for the Vickers microhardness (HV) method. A total of 240 indentations were created, with a spacing between centres of indentations of 0.2 mm, in a 10 (columns) x24 (rows) matrix. The indentation force was 1 kg (HV1), with a dwelling time of 10 s at the maximum force. An objective of 20X magnification was used.

2.6. Correlation analysis

To support the analysis of the influence of the microstructure features (including microhardness) of the samples on the Gaussian peaks forming the spectra of hydrogen released from the samples, the authors developed a new key correlation indicator the *microToH*. The development of this new key correlation indicator was pushed by the need to enhance and quantify the sensitivity and specificity of the interaction. When using other correlation coefficients, such as the coefficient of determination \mathbb{R}^2 or the Pearson correlation coefficient, the crossinfluence effects are easily over-saturated and not specific, disabling their application as a quantitative tool to support the analysis. Later, in §3.5, results will be presented for both the new *microToH* and the conventional Pearson correlation coefficients.

The *microToH* correlation coefficient is calculated based on Eq. (1).

$$microToH_{ij_norm} = \frac{microToH_{ij}}{\max(microToH_{i=1...4;j=1..6})}$$
(1)

The new key correlation coefficient: $microToH_{ij}$ is calculated based on Eq. (2). Note that Eq. (2) is the product between two parts, where the part 1 corresponds to the ratio of TDS feature variation versus microstructure feature variation \times penalizing weight for irrelevant feature variations.

$$microToH_{ij} = \frac{H_i}{micro_j} \min\left(H_i^2, \ micro_j^2\right)$$
(2)

The coefficients: H_i (TDS feature variation) and *micro_j* (microstructure feature variation) are calculated based on Eqs. (3) and 4, respectively. These dimensionless feature variation coefficients: H_i , and *micro_j*; establish the relevance of the difference between the feature (or property) assessed at NtS and Middle positions of the plate, versus the reference value of same feature assessed as representative of the transversal cross-section TD/ND.

$$H_i = \left(\frac{H_{N_t S} - H_M}{H_T}\right)_i \tag{3}$$

Where $i = [\text{peak } 1 \equiv 1; \text{ peak } 2 \equiv 2; \text{ peak } 3 \equiv 3; \text{ total hydrogen}$

concentration \equiv 4], H_{N_tS} is the median for hydrogen desorption feature *i* in set NtS, H_M is the median for hydrogen desorption feature *i* in set M, and H_T is the median hydrogen desorption feature *i* in set T (i.e. transversal sample depicted in Fig. 1).

$$micro_{j} = \left(\frac{microF_{N,S} - microF_{M}}{microF_{T}}\right)_{j}$$
(4)

Where *j* = [LAGB volume fraction \equiv 1; grain size (5°) \equiv 2; grain size

 $(15^{\circ}) \equiv 3$; microhardness $\equiv 4$; GND (low) $\equiv 5$, GND (high) $\equiv 6$], microF_{NtS} is the mean (or volume fraction) for microstructure feature *j* in area NtS, microF_M is the mean (or volume fraction) for microstructure feature *j* in area M, and microF_T is the mean (or volume fraction) for microstructure feature *j* in the transversal cross-section TD/ND (estimated indirectly from $2 \times \text{NtS} + 2 \times \text{Tr} + \text{M}$, as described in §2.3).

The Pearson correlation coefficient, r [44], as defined in Equation 5, was used to support the analysis of the relationship between the microstructure features and the spectra of hydrogen released from the three sample set positions.

$$r = \frac{\sum (microF_j - \overline{microF}) (H_i - \overline{H})}{\sqrt{\sum (microF_j - \overline{microF})^2 \sum (H_i - \overline{H})^2}}$$
(5)

Where *microF_j* is the microstructure feature value for observation *j*, \overline{microF} is the mean of the $microF_{j=1..6}$ values, H_i is the value of hydrogen desorption feature for observation *i*, and \overline{H} is the mean of the $H_{i=1..4}$ values.

3. Analysis of results

3.1. TDS results

TDS results of hydrogen measured from samples extracted from the studied steel, according to nomenclature in Fig. 1, are presented in Fig. 4.

Hydrogen concentrations attributed to peaks 1, 2, and 3, and for the total hydrogen concentration, were calculated for the samples of set NtS, set M and set T and the mean results for each set are summarized in Fig. 5 and Table 2. Hydrogen concentration of peak 1 is higher in set NtS and lower in set M. Hydrogen concentration of peak 2 is higher in set T and lower in set NtS. Hydrogen concentration of peak 3 is about the same for all three sets. Total hydrogen concentration is higher in set M and set T, and lower in set NtS. For the relatively small number of data points obtained from the hydrogen measurements, the median was considered for the correlation with the microstructure features since it's a better measure of the central tendency of the group as it is less sensitive to extreme values or outliers.



Fig. 4. TDS curves of desorbed hydrogen measured from set NtS, set M and set T samples of as-supplied 13CrMo4-5 steel.



Fig. 5. Mean hydrogen concentration, with indication of respective standard deviation, for peaks 1, 2 and 3, and for the total concentration (note the different scale) of the TDS curves measured for set NtS, set M and set T of specimens extracted from 13CrMo4–5 steel plate.

Mean \pm standard deviation and median of hydrogen concentrations of peaks 1, 2 and 3 and total hydrogen concentration of the TDS curves measured for set NtS, set M and set T. The median values are emphasized as they are the ones considered to establish the correlation with the microstructure features.

Hydrogen concentration [at.ppm]							
Near-to-surface (set NtS)		Middle (set M)		Transversal (set T)			
$\text{Mean} \pm \text{SD}$	Median	$Mean \pm SD$	Median	$Mean \pm SD$	Median		
1.84 ± 0.8	1.99	0.30 ± 0.08	0.26	0.90 ± 0.5	1.13		
0.75 ± 0.2	0.66	1.23 ± 0.53	1.16	1.78 ± 0.63	1.83		
0.67 ± 0.09	0.72	0.60 ± 0.16	0.65	0.69 ± 0.36	0.71		
3.55 ± 0.46	3.35	$\textbf{9.02} \pm \textbf{1.79}$	9.75	$\textbf{8.88} \pm \textbf{1.89}$	9.19		
	$\begin{tabular}{ c c c c } \hline Hydrogen concentral \\ \hline Near-to-surface \\ (set NtS) \\\hline \hline Mean \pm SD \\\hline 1.84 \pm 0.8 \\ 0.75 \pm 0.2 \\ 0.67 \pm 0.09 \\ 3.55 \pm 0.46 \\\hline \end{tabular}$	$\begin{tabular}{ c c c c } \hline Hydrogen concentration [at.ppm] \\ \hline Near-to-surface \\ (set NtS) \\ \hline Mean \pm SD & Median \\ \hline 1.84 \pm 0.8 & 1.99 \\ 0.75 \pm 0.2 & 0.66 \\ 0.67 \pm 0.09 & 0.72 \\ 3.55 \pm 0.46 & 3.35 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c } \hline Hydrogen concentration [at.ppm] \\ \hline Near-to-surface & Middle \\ (set NtS) & (set M) \\ \hline Mean \pm SD & Median & Mean \pm SD \\ \hline 1.84 \pm 0.8 & 1.99 & 0.30 \pm 0.08 \\ 0.75 \pm 0.2 & 0.66 & 1.23 \pm 0.53 \\ 0.67 \pm 0.09 & 0.72 & 0.60 \pm 0.16 \\ 3.55 \pm 0.46 & 3.35 & 9.02 \pm 1.79 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c } \hline Hydrogen concentration [at.ppm] & \\ \hline Near-to-surface & & Middle & \\ (set NtS) & & (set M) & \\ \hline Mean \pm SD & Median & & Median & \\ \hline 1.84 \pm 0.8 & 1.99 & 0.30 \pm 0.08 & 0.26 & \\ 0.75 \pm 0.2 & 0.66 & 1.23 \pm 0.53 & 1.16 & \\ 0.67 \pm 0.09 & 0.72 & 0.60 \pm 0.16 & 0.65 & \\ 3.55 \pm 0.46 & 3.35 & 9.02 \pm 1.79 & 9.75 & \\ \hline \end{tabular}$	$\begin{tabular}{ c c c } \hline Hydrogen concentration [at.ppm] \\ \hline Near-to-surface & Middle & Transversal (set NtS) & (set M) & (set T) \\ \hline Mean \pm SD & Median & Median & Median & Median & Mean \pm SD \\ \hline 1.84 \pm 0.8 & 1.99 & 0.30 \pm 0.08 & 0.26 & 0.90 \pm 0.5 \\ 0.75 \pm 0.2 & 0.66 & 1.23 \pm 0.53 & 1.16 & 1.78 \pm 0.63 \\ 0.67 \pm 0.09 & 0.72 & 0.60 \pm 0.16 & 0.65 & 0.69 \pm 0.36 \\ 3.55 \pm 0.46 & 3.35 & 9.02 \pm 1.79 & 9.75 & 8.88 \pm 1.89 \\ \hline \end{tabular}$		

Peak temperatures attributed to peaks 1, 2 and 3 were calculated for the samples of set NtS, set M, and set T, and are graphically depicted in Fig. 6. The yield statistically processed peak temperatures are summarised in Table 3.

3.2. DSC results

In order to understand if phase changes in the material influence hydrogen peaks in TDS, at certain temperatures, DSC measurements were performed. Fig. 7 shows the results from the complete heating and cooling cycle at a rate of 10 K/min. In accordance to [45,46], for ferritic-pearlitic microstructures, the Ac_{1s} refers to the beginning of the eutectoid reaction, where mostly pearlite transforms into austenite, and Ac₃ refers to the end of transformation of remaining ferrite into austenite. With similar procedure to the one used in [45,47,48,49], the Ac_1 and Ac_3 temperatures were extrapolated by applying a baseline correction, then tracing the baseline of the corrected peak and intersecting it with the tangent to the inflection point of the first endothermic peak, in order to find Ac1s, and intersecting the baseline with the end of the second endothermic peak, in order to find Ac₃. Fig. 8 depicts the implementation of this calculation procedure within the intercritical temperature region, i.e. [A₁, A₃] range. For the heating part of the DSC cycle, the calculated intercritical temperature region [1020, 1154] K is located at significantly higher temperature than the temperature range where hydrogen peaks occur {513, 633, 763} K, which means that the body centered cubic α iron to face centered cubic γ iron phase transformation between austenite onset temperature, A_{C1}, and austenite finish temperature, $A_{\text{C3}},$ is not the responsible mechanism for the hydrogen desorption obtained during the TDS testing.

Liu et al. [50], found that steel 13CrMo4–5 initially had the phases (Cr, Fe)₂₃C₆, (Cr, Mn)₂₃C₆, Cr₇C₃ and (Fe, Mn)₇C₃, and in the ferrite

grains, carbides of types M_3C , (Fe, $Mn)_3C$, (Fe, $Cr)_3C$, and M_6C . After long-term operation (550 °C for 23,000 h), where there are microstructure changes due to e.g. precipitation and transformation of carbides, decomposition of pearlite areas and changes in carbide morphology, the typical precipitates found at the grain boundaries were $M_{23}C_6$ and M_7C_3 , and within the grains were M_3C and (Fe, $Mo)_6C$ [50, 51]. Precipitation in 13CrMo4–5 already starts in fabrication and when in-service, at temperatures of 490–540 °C / 763–813 K and stress of about 50 MPa, different carbides start to precipitate over time [51]. In long-term operations, carbides like $M_{23}C_6$, M_7C_3 and M_3C , coarsen and grow in size, causing a decrease of loss of free carbon and also a change in the material's mechanical properties [50,52,53,54].

Fig. 9 shows the overlapping of the TDS results, with the DSC results obtained during heating part of the cycle. As main outcome from this procedure, the TDS peak 3 (from start to where it reaches maximum temperature), matches the precipitation region found via DSC, where the temperature domain of start of precipitation [763–813] K is emphasised by the blue region in Fig. 9.

3.3. SEM, EDX and EBSD results

SEM micrographs are shown in Fig. 10. The dark areas correspond to ferrite while the white lamellas in the pearlite microstructures are cementite. These carbon-enriched structures can also be found in small agglomerates at some grain boundaries, as shown in Fig. 10c, f and i.

The transversal cross-section TD/ND of the 13CrMo4–5 steel was studied using EDX to reveal the chemical composition of the nonmetallic inclusions (NMIs). NMIs with size from 20 μ m to 200 μ m were found to be SiO₂ particles (see Fig. 11a), while NMIs with size less than 5 μ m have a complex structure comprising O, Mg, Ca, and S (see Fig. 11b).



Fig. 6. Mean peak temperatures, with indication of respective standard deviation, of peaks 1, 2 and 3 of the TDS curves measured for set NtS, set M, and set T, of specimens extracted from 13CrMo4–5 steel plate.

Median peak temperatures of peaks 1, 2 and 3 of the TDS curves measured for set NtS, set M and set T.

	Peak temperature [K]					
	Near-to- surface (set NtS)	Middle (set M)	Transversal (set T)	Mean value		
Peak 1	509	515	521	515 ± 6		
Peak 2	628	635	640	634 ± 6		
Peak 3	760	764	763	762 ± 2		



Fig. 7. DSC measurements for 13CrMo4-5 at 10 K/min.



Fig. 8. DSC measurements for 13CrMo4–5, with inter-critical temperature region calculated at a rate of 10 K/min.



Fig. 9. Overlapping of DSC heating curve results, with TDS results of samples taken from all position sets, namely set NtS, set M and set T. Note that both TDS and DSC are implemented at 10 K/min heating rate.

EBSD analysis was performed at areas NtS, Tr and M (Fig. 3) of the steel plate transversal cross-section TD/ND. The EBSD results are collected in Fig. 12. Fig. 12 shows a minor anisotropy in grain shape caused by the hot working of the steel. The distribution of grain boundary misorientation angle was analysed for areas NtS, Tr and M using the misorientation map data as in Fig. 12d,e,f, respectively. Additionally, the IPF map for area NtS (Fig. 12a) shows a distinct texture, reflecting different dominant preferred crystal orientations, compared to the other areas (Fig. 12b and c).

Histogram plots shown in Fig. 13 reveal a comparable skewed distribution with the higher number of occurrences at about 50° of grain boundary misorientation angle.

The measurement data of grain boundary misorientation angle correspond to the individual pixels from the grain boundary misorientation maps shown in Fig. 12. Pixel size, at the same time, correspond to the step size of the EBSD analysis. It allows to define the $LAGB_{fraction}$ as defined in Eq. (6):

$$LAGB_{fraction} = \frac{(count_{LAGB} \cdot 100)}{count_{tot}}$$
(6)

Where $count_{LAGB}$ is the number of measurement data points within the grain boundaries with misorientation angles from 5° to 15° and $count_{tot}$ is the total number of measurement points within the grain boundaries for the complete misorientation angle range ~[5°, 62°]. The results are summarised in Table 4.

Grain boundaries play a significant role in hydrogen diffusion and trapping in steels and alloys facilitating the local accumulation of hydrogen and therefore working as the obstacle for further hydrogen diffusion beyond that grain boundary, depending on steel chemical

Area NtS



Area Tr



Area M



Fig. 10. SEM micrographs of etched 13CrMo4–5, of transversal cross-section TD/ND at different areas with different magnifications, and nomenclature of the locations in according to Fig. 2: (a) x1000 micrograph of area NtS; (b) x2000 micrograph of area NtS; (c) x4000 micrograph of area NtS; (d) x1000 micrograph of area Tr; (e) x2000 micrograph of area Tr; (g) x1000 micrograph of area M; (h) x2000 micrograph of area M; (i) x4000 micrograph of area M.

composition and phase structure [55,56,57]. Linear intercept method was used to define the grain size in the studied steel (ASTM E1382). Measurement results were obtained for areas NtS, Tr and M of the steel plate transversal cross-section TD/ND. Total measurement results distribution considering the threshold misorientation angle to be 5° and 15° through the steel plate transversal cross-section TD/ND is shown in Fig. 14. Table 5 presents the mean grain size of threshold misorientation angles 5° and 15° for areas NtS, Tr and M, and for transversal cross-section TD/ND.

The aim in investigating the grain size is to aid the comparative study

of grain boundary area between the different areas of the steel transversal cross-section TD/ND. Considering that grain size is inversely proportional to the grain boundary area, the goal is to find the trend or correlation between the grain size and hydrogen concentration associated with a specific hydrogen peak corresponding to one trapping site group, with characteristic trapping energy. As shown in Fig. 14, in all three areas, the grain size distribution exhibits a skewed pattern, with a higher frequency of smaller grain sizes, suggesting a Weibull-like distribution rather than a symmetrical one. The mean grain size of threshold misorientation angles 5° and 15° is 9 % and 12 %,



Fig. 11. SEM micrographs with corresponding EDX spectroscopy analysis of NMIs observed in the studied 13CrMo4-5 steel.



Fig. 12. EBSD results at transversal cross-section TD/ND of 13CrMo4–5 steel, with inverse pole figure (IPF) maps taken at areas NtS (a), Tr (b), and M (c). Low-angle grain boundaries and high-angle grain boundaries are highlighted by red and black colour lines, respectively, in IPF maps (a)-(c). Grain boundary misorientation maps taken at areas NtS (d), Tr (e) and M (f). Step size 0.5 μm.

respectively, higher in area M compared to area NtS, which means the latter has a higher number of grain boundaries than the former.

EBSD measurement results obtained from areas NtS, Tr and M of the steel transversal cross-section TD/ND were processed to define the GND density and adaptive DMM with threshold misorientation angle $\Delta \theta = 0$. 5° and $\Delta \theta = 2^{\circ}$ [43]. GND density map and adaptive DMM maps are shown in Fig. 15.

Comparative analysis of GND density distribution for areas NtS, Tr and M of the steel transversal cross-section TD/ND is shown in Fig. 16. Fig. 16 shows the number of times (count) a certain GND density appears. Table 6 presents the counts per area and per density range. It also includes counts per total number of measurement points, i.e. counts per pixel, where the total number of measurement points for areas NtS and M is 374 (horizontal pixels) x 280 (vertical pixels) = 104720 pixels, and



Fig. 13. Distribution of misorientation angle data analysed for areas NtS (a), Tr (b), and M (c) areas considering the total measured range [5°, 62°] of the misorientation angle data.

Results from Eq. (6) for areas NtS, Tr, M, and transversal cross-section TD/ND areas (step size 0.5 μ m).

	Near-to- surface (area NtS)	Transition (area Tr)	Middle (area M)	Transversal cross- section TD/ND area
<i>count_{tot} count_{LAGB}</i> LAGB volume fraction [%]	19896 1254 6.3	19768 1389 7.03	18165 1392 7.66	95890 6678 6.96

for transversal cross-section TD/ND area is 374 (horizontal pixels) x 1400 (vertical pixels) = 523600.

In the GND low, i.e. with density range from 1×10^{13} to 5×10^{13} μm^{-1} , the area NtS contains higher counts compared to that in areas Tr and M of the transversal cross-section TD/ND, as shown in Fig. 16. GND low corresponds to about 55 % of the GND density map. For the GND high, i.e. with density range above 5×10^{13} μm^{-1} , the counts at area M are higher compared to that calculated at areas NtS and Tr of the transversal cross-section. GND high corresponds to about 15 % of the full GND density map.

Individual grain analyses revealing the correlation of the graphical

representation of GND density maps and the adaptive DMM maps are shown in Fig. 17, Fig. 18 and Fig. 19. All grains were taken from the area Tr. The observed behaviour of GND density distribution shows a certain correlation with results of adaptive DMM analysis, as emphasized by the arrows. GND density map visualized for the range between 1×10^{13} and $5\times10^{13}\,\mu\text{m}^{-1}$ and for the range above $5\times10^{13}\,\mu\text{m}^{-1}$ correlate with the deformation pattern of adaptive DMM calculated with $\Delta\theta=0.5$ ° and $\Delta\theta=2$ °, respectively.

The individual grains rarely contain both deformation density levels distinguished clearly within one grain as shown in Fig. 17. A major part of the analysed grains reveals preferably the only one deformation density level associated with the GND density from 1×10^{13} to 5×10^{13} μm^{-1} or above 5×10^{13} μm^{-1} . The adaptive DMM map calculated with $\Delta\theta=2$ ° for the grain shown in Fig. 18 evidences the maximum misorientation of about 0.25°. The observed misorientation map has a good correlation with GND density map from 1×10^{13} to $5\times10^{13}\,\mu m^{-1}$, i.e. the location of highest GND density matches the location of the highest misorientation values given by adaptive DMM. However, one has to have in mind the limitations and sensitivity of GND density calculations from EBSD data when evaluating correlations between the different methods, like the influence of step size, the measurement noise, precision of the measured orientations, among others, on the calculations [36,58,59,60].



Fig. 14. Grain size distribution for areas NtS (a), Tr (b), and M (c) of the steel plate transversal cross-section TD/ND.

Mean grain size of threshold misorientation angles 5° and 15° for areas NtS, Tr, and M areas, and for transversal cross-section TD/ND.

	Near-to- surface (area NtS)	Transition (area Tr)	Middle (area M)	Transversal cross- section TD/ND area
Mean grain size with threshold misorientation angle 5°	15.3	15.5	16.7	15.6
Mean grain size with threshold misorientation angle 15°	16.5	16.7	18.4	17.0

For detailed analysis of the deformation structures, the step size of EBSD scanning was decreased from 0.5 µm to 0.1 µm. The higher resolution adaptive DMM and GND maps analysed for individual grains reveals the same correlation behaviour as shown in Fig. 19. The well-distinguished deformation structures at GND density map for the range above $5 \times 10^{13} \,\mu m^{-1}$ (see Fig. 19b) are clearly associated with misorientation starting from about 0.8° (see Fig. 19a) while GND density map for the range from 1×10^{13} to $5 \times 10^{13} \,\mu m^{-1}$ (see Fig. 19d) shows a good match with misorientation of about 0.3° (see Fig. 19c), however the noise level is still quite extensive for low deformations.

The eventual coercive effect of pearlite structures on the deformation pattern of the ferrite structures was also investigated using a quantitative analysis of the adaptive DMM maps. Fig. 20a,b depicts some zones

with accumulation of the deformation of the ferrite structures in vicinity of the pearlite structures. The sensitive analysis, via two different misorientation angle thresholds (namely, $\Delta \theta = 0.5^{\circ}$ versus $\Delta \theta = 2^{\circ}$), aims at emphasizing this boundary phenomenon. The perlite grains are (frequently) found to act as boundary promoting the accumulation of the ferrite grains with higher levels of misorientation. This boundary phenomenon includes multidirectional effect, namely at the vicinity of curved perlite grains surrounding a ferrite domain. This phenomenon, that is quite generalized and therefore not so evident on the plot with lower misorientation threshold $\Delta \theta = 0.5^{\circ}$, is then emphasized in the plot with higher misorientation threshold $\Delta \theta = 2^{\circ}$ This analysis was performed in the area Tr, and the pearlitic structures are emphasized by white dashed lines in Fig. 20a,b. The identification of the different microstructures is supported by the micrograph in Fig. 20c.

3.4. Microhardness results

Measurement of microhardness was performed at the 13CrMo4–5 steel transversal cross-section TD/ND forming a map of microhardness distribution, as shown in Fig. 21. The result evidences the non-uniform microhardness distribution with a harder area NtS and softer area M of the steel transversal cross-section TD/ND. It also evidences the quasi-symmetric results obtained from the microhardness measurements of the whole transversal cross-section TD/ND area. The distribution of the microhardness measurements is shown in Fig. 22. The distribution contains 73 %, 68 % and 80 % of observations within one standard deviation limit for areas NtS and M and for the whole transversal cross-section TD/ND, respectively. The results of mean and standard deviation



Fig. 15. GND density (line 1) and adaptive domain median misorientation (DMM) maps calculated with $\Delta \theta = 0.5^{\circ}$ (line 2) and 2° (line 3) reveal the deformation structures in areas NtS, Tr and M of the studied 13CrMo4–5 steel transversal cross-section TD/ND.



Fig. 16. GND density distribution from 1×10^{13} to $15 \times 10^{13} \ \mu m^{-1}$ compared for areas NtS, Tr and M of the 13CrMo4–5 steel transversal cross-section TD/ND. The GND density was split into two density ranges: from 1×10^{13} to $5 \times 10^{13} \ \mu m^{-1}$ (GND low) and above $5 \times 10^{13} \ \mu m^{-1}$ (GND high).

Counts and counts per pixels for GND low and GND high for areas NtS and M, and for the transversal cross-section TD/ND area.

		Near-to- surface (area NtS)	Middle (area M)	Transversal cross-section TD/ND area
GND low	Counts Counts per pixels	49300 0.47	43752 0.42	235122 0.45
GND high	Counts Counts per	11546 0.11	11558 0.11	61024 0.12
	pixels			

calculations are summarised in Table 7.

The mean of the whole transversal cross-section TD/ND was calculated via two methods:

- by averaging the 240 microhardness values of the 10 (columns) × 24 (rows) matrix;
- by considering that the mean microhardness of the transversal crosssection TD/ND corresponds to $2 \times NtS + 2 \times Tr + M$, established in §2.3 and applied to the remaining microstructure features.

The equal results for the mean of the whole transversal cross-section TD/ND obtained by these two methods (Table 7) and the quasi-symmetric results shown in Fig. 21 indicate the suitability of considering that the transversal cross-section TD/ND corresponds to $2 \times \text{NtS} + 2 \times \text{Tr} + \text{M}$, for the remaining microstructure features.

3.5. Relationship between TDS and microstructure analysis results

For the large number of data points obtained for each of the considered microstructure features (grain size and microhardness), the mean was considered. For the relatively small number of data points obtained from the hydrogen measurements (i.e., three points), the median was considered since it's a better measure of the central tendency of the group.

Table 8 compiles all the data that will be used to evaluate the hydrogen-as-a-probe applied in the characterisation of samples from different positions presents the results of the median hydrogen measurements, LAGB volume fraction and mean or count of the microstructure features.

The locations of TDS sample extraction are the sets NtS, M and T, according to Fig. 1. The microstructure features (LAGB volume fraction, grain size, microhardness, and GND) are obtained at the areas NtS, M and transversal cross-section TD/ND, according to Fig. 3. The correspondence considered between the TDS and microstructure features in the correlation analysis is as follows:

- The sample set NtS corresponds to the area NtS: set NtS = area NtS;
- The sample set M corresponds to the area M: set $M \equiv area M$;
- The sample set T corresponds to the area of the whole transversal cross-section TD/ND = microstructure features from 2 × near-to-surface area + 2 × transition area + middle area: set T \equiv transversal cross-section TD/ND.

The TDS peak values and total hydrogen concentration, presented in Table 8 for the different specimen locations, were previously discussed in the analysis of the results presented in §3.1. Table 8 also encompasses the different areas of interest in the evaluated microstructure features, presented in §3.3 and §3.4.

Fig. 23 presents the comparison between values from set NtS and from M, for the median hydrogen measurements, LAGB volume fraction, and mean or count per pixel of microstructure features.

Concerning the hydrogen concentration features, the Peak 1 values are higher in set NtS ($H_1 = 1.33$). Peak 2 ($H_2 = -0.62$) and total hydrogen concentration ($H_4 = -0.62$) values are higher in set M. Peak 3 is not affected by location since $H_3 = -0.01$.

Concerning the microstructure features, the values of LAGB volume fraction (*micro_{LAGB}* = -0.2) and grain size of threshold misorientation angle of 5° (*micro_{Grain}* size 5 = -0.09) and 15° (*micro_{Grain}* size 15 = -0.11) are higher in area M. Microhardness (*micro_{Hardness}* = 0.05) and GND density in the range from $1 \times 10^{13} \,\mu\text{m}^{-1}$ to 5×10^{13} (*micro_{GND}* high = 0.12) values are higher in area NtS. GND density in the range above $5 \times 10^{13} \,\mu\text{m}^{-1}$ is not affected by location since *micro_{GND}* high = 0.

Table 9 presents the results of correlation analysis, using the correlation coefficients established in $\S2.5$, namely *microToH* and Pearson, r.

Fig. 24 presents the values of the microToH correlation coefficient, and Fig. 25 presents the values of the Pearson correlation coefficient r. These results will be discussed in chapter 4, but it is immediately noticeable that the Pearson correlation coefficient r, although in trend agreement with the new proposed microToH correlation coefficient, the r is less capable to address the physics of the influence of the microstructure from the samples in different locations in the hydrogen desorption peaks. As example, the peak 3 presents a negligible variation of 1 %, but nevertheless the Pearson correlation coefficient identifies that peak 3 is very strongly influenced by GND high (r = 1). Another significant limitation of the Pearson correlation coefficient is that it saturates the capacity of distinguish between different levels of influence. Example is that according to the Pearson correlation coefficient, the peak 1 is very strongly influenced by almost all microstructure features ($|\mathbf{r}| > 0.98$). This proves the need for a more sensitive and specific correlation coefficient, that the authors strive to set via the new proposed microToH correlation coefficient, formulated in §2.5. The values of the Pearson correlation coefficient r are not going be considered in the following discussion.

According to the results of *microToH*, the highest influence by a microstructure feature on peak 1 is the LAGB volume fraction, setting the standard value, i.e. microToH = -1. This result reads that the highest the local LAGB volume fraction, the lower the hydrogen desorption at the conditions of peak 1, namely at the vicinity of 515 K. But the influence of the LAGB on TDS features, needs be considered in parallel with the other relevant microstructure features. This holistic analysis is implemented on the discussion of the correlation between hydrogen measurements and microstructure features and presented in the next chapter.



Fig. 17. Individual grain analysis shows the adaptive DMM map calculated with $\Delta \theta = 2$ ° (a) and $\Delta \theta = 0.5$ ° (c), and GND density map considering the GND density range above $5 \times 10^{13} \,\mu m^{-1}$ (b) and from 1×10^{13} to $5 \times 10^{13} \,\mu m^{-1}$ (d). Area Tr, step size 0.5 μm .



Fig. 18. Individual grain analysis shows the adaptive DMM map calculated with $\Delta \theta = 2$ * (a) and GND density map considering the GND density range from 1×10^{13} to $5 \times 10^{13} \mu m^{-1}$ (b). Area Tr, step size 0.5 μ m.



Fig. 19. Individual grain analysis shows the high resolution adaptive DMM map calculated with $\Delta \theta = 2^{\circ}$ (a) and $\Delta \theta = 0.5^{\circ}$ (c), and GND density map considering the GND density range above $5 \times 10^{13} \,\mu\text{m}^{-1}$ (b) and from 1×10^{13} to $5 \times 10^{13} \,\mu\text{m}^{-1}$ (d). Area Tr, step size 0.1 μ m.



Fig. 20. Adaptive DMM maps calculated for $\Delta \theta = 0.5^{\circ}$ (a) and $\Delta \theta = 2^{\circ}$ (b), and corresponding SEM micrograph (c). Dashed white lines emphasize the location of perlite structures.

4. Discussion

Analysis of the hydrogen desorption features per set of TDS sample locations (set M versus set NtS)

The formulation of the TDS features sensitivity to the sample location, between the set NtS (near-to-surface) and the set M (middle), was established in Eq. (3), and it is plotted in Fig. 23, as H_i , with i = 1 peak 1; i = 2 peak 2; i = 3 peak 3; and i = 4 standing for total hydrogen concentration.

Hydrogen desorption values associated with peak 1 (located at about 515 K, as presented in Table 3) are 133 % higher in set NtS than in set M ($H_1 = 1.33$). In the opposite sensitivity direction, and with only about

the intensity of the difference found for peak 1, the hydrogen desorption values associated with peak 2 (located at about 634 K) are 62 % higher in set M than in set NtS ($H_2 = -0.62$). As peak 2 is the major contributor to the total hydrogen concentration, as seen in §3.5, the total hydrogen concentration values are also higher in set M, than in set NtS, and with similar intensity as presented in the sensitivity analysis of peak 2 ($H_4 = -0.62$). Hydrogen desorption values associated with peak 3 (located at about 762 K) present a negligible sensitivity to the location of the sample sets ($H_3 = -0.01$), meaning that this peak, found in §3.2 to be related with carbide precipitation phenomena, is not influenced by the location of the sample.

Kawakami and Matsumiya [61] attributed a peak at \sim 400 K to hydrogen trapped at the cementite/ferrite interface and a peak at 500 K



Fig. 21. Microhardness measurement performed at transversal cross-section TD/ND of 13CrMo4-5 steel by Vickers micro indentation method (HV1).



Fig. 22. Microhardness measurement distribution in the area NtS (a), and area M (b), and in the whole transversal cross-section TD/ND area (c).

 Table 7

 Mean and standard deviation microhardness for areas NtS, Tr and M, and for the transversal cross-section TD/ND area.

Microhardness [HV1]	Near-to-surface (area NtS)	Transition (area Tr)	Middle (area M)	Transversal cross-section TD/ND area (240 matrix values)	Transversal cross-section TD/ND area (2×NtS+2×Tr+ <i>M</i>)
Mean \pm standard deviation	144 ± 4	138 ± 4	137 ± 2	140 ± 5	140 ± 4

to the migration energy from the defects, such as grain boundaries in cementite due to deformation, in bcc-Fe. A study on hydrogen desorption in deformed pearlitic steel attributed a peak at ~450 K, for 5 K/min heating rate, i.e. half of the value in the present investigation, to the desorption of hydrogen at vacancies, dislocations, and coherent ferrite/cementite interfaces [62]. The same study also shows findings of a hydrogen desorption peak at ~600 K exclusively present in the deformed pearlitic steel, compared to undeformed steel [62], which the authors attributed to strained ferrite/cementite interfaces and/or defects within the cementite. Yamasaki et al. [63] concluded that a peak at \sim 300 °C \approx 573 K could only be seen in cold-worked steel, quenched high-carbon steel and steels containing dissolved carbon like as-quenched martensite, and was associated with hydrogen trapped at the dislocation core. Yamabe et al. [64] concluded that in hydrogen-exposed low-alloy steel, two peaks were observed at ~ 100 °C \approx 373 K and \sim 400 °C \approx 673 K, whereas in non-hydrogen-exposed samples, only the 600 K one appeared. Another study on iron using low-temperature TDS (from -200 °C to 200 °C) concluded that a peak at ${\sim}35~^\circ\text{C}\approx308$ K and a peak at ${\sim}85~^\circ\text{C}\approx358$ K were associated with dislocations and high-angle grain boundaries, respectively [65].

Analysis of the microstructure features at areas of interest

The formulation of the microstructure features sensitivity to the sample location, between the set NtS (near-to-surface) and the set M (middle), was established in Equation 4, and it is plotted in Fig. 23, as *micro_j* with j = [LAGB; Grain size (5); Grain size (15); Hardness; GND low; and GND high].

LAGB can be considered as preferable trapping sites for diffusible hydrogen due to its composition of recombined walls of high dislocation density [62,66,67]. HAGB, which evolved from LAGB due to increased deformation levels, have higher hydrogen trap density by providing a larger number of hydrogen traps and, therefore, decrease the hydrogen diffusivity in the material [68,69]. Note that as the defined HAGB includes grain boundaries with misorientation angles over 15° , it also encompasses a transition between LAGB and HAGB. In this steel 13CrMo4–5, the LAGB volume fraction represents roughly 7% of the grain boundaries at the cross-section, according to Table 4, while the rest comprises HAGB. This is 20 % higher in area M compared to area NtS (*micro_{LAGB}* = -0.20). This is the major variation among all assessed microstructure features.

Grain size with a threshold misorientation angle of 5° includes both

The results of the median hydrogen measurements and different microstructure features studied for NtS, M and cross-section TD/ND.

		Near-to- surface set NtS ≡ area NtS	Middle set M≡ area M	Total cross- section set T ≡ transversal cross-section TD/ND
Median	Peak 1 [at.ppm]	1.83	0.25	1.19
	Peak 2 [at.ppm]	0.66	1.65	1.60
	Peak 3 [at.ppm]	0.72	0.73	0.88
	Total hydrogen concentration [at. ppm]	3.35	9.75	9.19
Volume fraction	LAGB volume fraction [%]	6.30	7.66	6.96
Mean	Grain size (5) [µm]	15.3	16.7	15.6
	Grain size (15) [µm]	16.5	18.4	17
	Hardness [HV1]	144	137	140
Counts per	GND low	0.47	0.42	0.45
pixel	GND high	0.11	0.11	0.12



Fig. 23. H_i and *micro_j* coefficients, based on Eqs. (3) and (4), respectively, and obtained from hydrogen desorption features $i = [\text{peak } 1 \equiv 1; \text{peak } 2 \equiv 2; \text{peak } 3 \equiv 3;$ total hydrogen concentration $\equiv 4]$ and microstructure features $j = [\text{LAGB volume fraction} \equiv 1; \text{Grain size } 5 \equiv 2; \text{Grain size } 15 \equiv 3; \text{Hardness} \equiv 4;$ GND low $\equiv 5$, GND high $\equiv 6]$.

Table 9

Results of correlation coefficients: microToH and r (Pearson), between median hydrogen peaks and total concentration and microstructure features.

		Peak 1	Peak 2	Peak 3	Total hydrogen concentration
LAGB volume	microToH	-1.00	0.47	0.00	0.46
fraction	r	-1.00	0.88	0.04	0.87
Grain size (5)	microToH	-0.46	0.21	0.00	0.21
	r	-0.98	0.72	-0.23	0.70
Grain size (15)	microToH	-0.56	0.26	0.00	0.26
	r	-0.98	0.71	-0.25	0.69
Hardness	microToH	0.26	-0.12	0.00	-0.12
	r	0.98	-0.92	-0.14	-0.91
GND low	microToH	0.60	-0.28	0.00	-0.28
	r	1.00	-0.84	0.05	-0.82
GND high	microToH	-0.01	0.00	0.00	0.00
	r	0.09	0.47	1.00	0.49

LAGB and HAGB, while grain size with a threshold misorientation angle of 15° includes mostly HAGB. The grain size is inversely proportional to the grain boundary area, which is a hydrogen trapping site [62,65,67, 69]. According to Table 5, the mean grain sizes are 15.6 µm and 17.0 µm

for grains with a threshold misorientation angle of 5° and 15°, respectively. Area NtS has 9% and 11% smaller mean Grain size (5) and Grain size (15), respectively (*micro*_{Grain} size (5) = -0.09, and *micro*_{Grain} size (15) = -0.11). Thus, the area NtS has consequently a higher number of grain boundaries. The microhardness at area NtS is 5% higher compared to area M (*micro*_{Grain} size (5) = 0.05). This agrees with the Hall–Petch effect, which reflects the inverse relationship between grain size and strength/hardness of metals [70].

Area NtS also shows a different texture compared to the other areas, as shown in Fig. 12. Preferred crystal orientation can impact hydrogen uptake, influencing hydrogen transport and permeation properties. Different crystal planes display varying hydrogen absorption energies and diffusion rates [71,72]. The Hall–Petch effect has been shown to increase with texture intensity, i.e. texture intensity enhances the material strength observed from the decrease in grain size [73].

The mapping view of the low and high GND density range corresponds well to adaptive DMM analysis performed for misorientation angles of 0.5° and 2°, respectively, evidencing a specific origin of the observed defects corresponding apparently to dislocation cell structures and sub-grain structures formation. The minimum misorientation values across dense dislocation walls and sub-grain boundaries are specified to be 0.5° and 2° , respectively, as proposed by Lehto [43], and based on direct TEM measurements performed on pure iron by Tao et al. [74]. GND low corresponds to about 45 % of the steel cross-section TD/ND, with 12 % higher counts per pixel of GND low density in area NtS versus the area M (micro_{GND low} = 0.12). This is the second major variation among all the microstructure features, meaning that area NtS has significantly more dislocations than area M. Increased dislocation density (below the deformation threshold to form new grain structures) generally leads to increased strength in metals. These results are in accordance with higher microhardness in area NtS, which can be attributed to influence of grain size, texture and dislocation density. GND high corresponds only to about 12 % of the steel cross-section TD/ND. GND high is not influenced by the sample location, as the difference between sets M and NtS is null (*micro*_{GND high} = 0).

Correlation between hydrogen measurements and microstructure features The interaction between the TDS features and microstructure features in assessing the sensitivity to the sample location, between the set NtS (near-to-surface) and the set M (middle), was established in Eqs. (1) to 4, and it is plotted in Fig. 26, as *microToH*.

From the results, there are one TDS feature, and one microstructure feature, that promptly show to have null contribution for the correlation analysis. These are: i) the GND high, for which the counts are not influenced by the sample location, and the amount is not very significant in any of the areas (11 to 12 %, in according to Table 6), and therefore it also has no influence in any of the three peaks and total hydrogen concentration; and ii) Peak 3 of hydrogen TDS (located at about 762 K), which based on DSC measurements (Fig. 9), corresponds to the region of the beginning of precipitation of carbides containing metallic elements like Fe, Cr and Mo. It can be assumed that the precipitation of carbides in the steel is the mechanism responsible for the desorption of hydrogen is trapped inside carbides, at their interfaces or is simply released due to the electrochemical and thermodynamic evolutions inherent to the carbide precipitation phenomena.

Peak 1 is the TDS feature most influenced by the microstructure features. The highest influence on peak 1 is from the LAGB volume fraction, setting the standard value (*microToH* = -1). In same inverse, or negative, correlative influence, it is possible to find the grain size with a threshold misorientation angle of 5°, presenting a *microToH* = -0.46, and 15°, presenting an even higher value of *microToH* = -0.56. In direct correlative influence the low density GND presents a very relevant value of *microToH* = 0.6, and the hardness a lower value of *microToH* = 0.26. Since Grain size (5) includes both LAGB and HAGB, and Grain size (15) is associated mostly with HAGB, and GND low are associated with



Fig. 24. Correlation analysis using microToH between median of hydrogen concentration of Gaussian peaks 1, 2 and 3, and total hydrogen concentration, and LAGB volume fraction, mean grain size of threshold misorientation angle of 5° and 15°, mean microhardness and counts per pixel for GND density calculated for the range from 1×10^{13} to $5 \times 10^{13} \,\mu\text{m}^{-1}$ (low) and for the range above $5 \times 10^{13} \,\mu\text{m}^{-1}$ (high).



Fig. 25. Pearson correlation matrix between median of hydrogen desorption of Gaussian peak 1, 2 and 3, and total hydrogen desorption concentration, and LAGB volume fraction, mean grain size of threshold misorientation angle of 5° and 15°, mean microhardness and counts per pixel for GND density calculated for the range from 1×10^{13} to $5 \times 10^{13} \,\mu\text{m}^{-1}$ (low) and for the range above $5 \times 10^{13} \,\mu\text{m}^{-1}$ (high).

dislocations, then these results are coherent and corroborate well with previous findings. The results strongly suggest that hydrogen desorption associated with peak 1 (at 515 K) is associated with large number of dislocations (GND low) and higher number of grain boundaries (inherent to the smaller grain size), preferentially associated with HAGB.

Peak 2 and total hydrogen concentration (that is mostly governed by the contribution of peak 2), presents a clear opposite correlative effect with the microstructure features, when compared with the correlation results obtained for the peak 1. This means that peak 2 is strongly governed by LAGB volume fraction (*microToH* = 0.47) and more weakly influenced by the remaining microstructure features assessed in this correlation analysis. In summary, the higher content of LAGB, of the slightly larger and softer grain and at the middle area of the plate, resulted in higher hydrogen desorption content at the peak 2 temperature of about 634 K. There is no clear indication from these results that hydrogen desorption associated with peak 2 is related to dislocations or sub-grain boundaries, apart from the influence of deformation found in literature publications [62,63,64].

5. Conclusions

From the analysis of the influence of the location of extraction of samples, from a 5 mm plate of 13CrMo4–5 plate, on the highly sensitive TDS spectra, the main conclusion is that the sample location has a

significant influence in some of the features, and therefore it needs to be considered as one relevant aspect in the research plan.

The main features of the TDS spectra are the hydrogen content and temperature of the Gaussian peaks forming the spectra, and the total hydrogen concentration. The most impacted feature of the TDS spectra by the location of extraction of samples is the hydrogen desorption of the peak 1, located at about 515 K. The hydrogen desorbed intensity of peak 1 of the sample location set NtS (near-to-surface) was 1.83 at.ppm, versus the 0.25 at.ppm obtained from the set M (middle), and with the set T (transversal cross-section TD/ND reaching an intermediate value of 1.19 at.ppm. These conditions yield a relative normalized difference of 133 % between set NtS and set M, in terms of the influence on peak 1. From the correlation analysis with microstructure features, the large number of dislocations (GND low), different texture and higher number of grain boundaries were found to be the most influential features driving these results at peak 1.

The location of extraction of samples also has a relevant role in the total hydrogen concentration via the influence on the hydrogen desorption values of peak 2 located at about 634 K. The total hydrogen concentration of the sample location set NtS (near-to-surface) was 3.35 at.ppm, versus the 9.75 at.ppm obtained from the set M (middle), and with the set T (transversal cross-section TD/ND reaching an intermediate value of 9.19 at.ppm. These conditions yield a relative normalized difference of 62 % between set NtS and set M, in terms of the influence on total hydrogen concentration. From the correlation analysis with

microstructure features, the higher content of LAGB, of the slightly larger and softer grain at the middle area of the plate, resulted in higher total hydrogen concentration.

The location of extraction of samples has negligible role in the hydrogen desorption values associated with peak 3 located at about 762 K. Based on the DSC analysis, this peak 3 was found to be related with the first exothermic peak of the heating cycle associated with carbide precipitation phenomena. The hydrogen desorption at the peak 3 temperature domain is therefore influenced by the chemical composition and not by the location of extraction of the sample.

A new correlation coefficient was formulated, the *microToH*, replacing the typical Pearson correlation coefficient r. The new correlation coefficient proved to be a more sensitive and specific tool supporting the relation between the TDS and the microstructure features.

In support of the analysis of the deformation structure, and validation of the considered GND density ranges, high resolution adaptive DMM and GND maps were analysed at individual grains. From the individual grain analysis performed in the Tr (transition) area, i.e. between the NtS and M domains, the maps shown to be in agreement, and the high resolution adaptive DMM evidences the accumulation of the deformation in the ferritic domain at the vicinity of the pearlite structures, with the pearlite structure exhibiting considerably smaller deformation compared to that in its surroundings.

Appendix A. Estimated angular measurement noise

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CRediT authorship contribution statement

Maria I. Silva: Conceptualization, Investigation, Writing – original draft, Writing – review & editing, Visualization. Evgenii Malitckii: Conceptualization, Investigation, Visualization, Writing – original draft, Writing – review & editing. Pauli Lehto: Software, Writing – review & editing. Pedro Vilaça: Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 26. Estimated angular measurement noise for 4000x and 2000x SEM magnification.

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