Determination of the equivalent hydrogen fugacity during electrochemical charging of 3.5NiCrMoV steel

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Highlights

- A new thermal desorption spectroscopy (TDS) apparatus was used to study hydrogen in a 3.5NiCrMoV steel
- The hydrogen concentration increased with increasingly negative charging potential and increasing hydrogen gas pressures.
- The equivalent hydrogen fugacity versus charging overpotential relationship was derived.
- A two-site model for Sieverts' Law explained the positive Y-intercept, as the density of already filled hydrogen traps.

ABSTRACT

A new thermal desorption spectroscopy (TDS) apparatus was used to identify the hydrogen trapping peaks, and to measure the hydrogen concentrations in 3.5NiCrMoV steel after hydrogen charging electrochemically, and in gaseous hydrogen. The hydrogen concentration increased with (i) increasingly negative charging potential and (ii) increasing hydrogen gas pressure. The equivalent hydrogen fugacity versus charging overpotential was derived. There was a difference in the diffusible hydrogen traps activated during electrochemical and gas phase charging, attributed to the difference in the hydrogen fugacity. A two-site model for Sieverts' Law explained the positive Y-intercept, as the density of already filled hydrogen traps.

Keywords: A. steel, B. TDS, C. hydrogen embrittlement

1. Introduction

Hydrogen is considered a future clean energy vector [1, 2] that can be used as an intermediate between a primary green energy source like solar energy, and secondary electricity production, for example in a fuel cell. A challenge for the hydrogen economy is finding inexpensive materials that can safely store hydrogen gas [3, 4]. Several steels have been proposed for hydrogen gas storage, including ASTM A106 Grade B, API 5L Grade X42, X52 and 34CrMo4 [3]. The quench-and-tempered 34CrMo4 is a commonly-used steel, due to its reliability and strength. Recently, some medium strength steels, such as Ni-Cr-Mo steels, have been considered as possibly suitable for hydrogen gas storage [5]. Such medium-strength steels have tensile strengths in the range of 600–1000 MPa [6], are relatively inexpensive, and also find applications in the automotive, structural and construction industries [7-10].

Steels can be susceptible to hydrogen embrittlement (HE), such as the conventional high-strength steels [11-20], the advanced high-strength steels [21-32], and the medium-strength steels [6, 33-40]. HE occurs when the load-bearing steel interacts with a critical amount of hydrogen, which is often of the order of a few wt ppm ($\mu\text{g g}^{-1}$). HE can cause sub-critical crack growth and unexpected fracture, and significant loss of strength, toughness and ductility [41-43]. Sub-critical crack growth occurs above a threshold stress, or above an applied threshold stress intensity factor. Sub-critical crack growth continues until a critical crack size is reached, where upon fast fracture is expected, because the fracture toughness has been exceeded. Alternatively, hydrogen embrittlement can cause some reduction in ductility without decreasing strength and without causing sub-critical crack growth.

Some steels that might be considered for the hydrogen economy were found to be susceptible to HE [44-46]. Recently, Liu et al. used the linearly increasing stress test (LIST) [47] to study HE susceptibility in 3.5NiCrMoV [48] and other Ni-Cr-Mo medium-strength steels [49] proposed for hydrogen gas storage. They observed no sub-critical crack growth, but there was some HE susceptibility in these steels. The HE was manifested by some reduction in ductility and the presence of some brittle features on the fracture surface. They

also noted that inclusions decreased the HE resistance of these steels, which highlights a benefit of using clean steels for hydrogen gas applications.

Hydrogen can be trapped by lattice defects [50]. Traps increase hydrogen solubility, decrease diffusivity [51, 52], and can enhance or diminish HE susceptibility [53, 54]. Reversible or weak traps can act as a hydrogen source, and supply diffusible hydrogen to highly stressed sites in the lattice to cause HE [55]. Conversely, the presence of well-distributed irreversible traps could reduce the HE vulnerability of the steel, especially if only a finite amount of hydrogen is available [32, 56-61]. It is thus important to study hydrogen-trap interactions to better understand HE susceptibility in medium strength steels.

Thermal desorption spectroscopy (TDS) is a powerful technique to study hydrogen-trap interactions. TDS typically measures the amount of hydrogen desorbed from a specimen subjected to controlled heating [62-65]. TDS can (i) measure low hydrogen concentrations at ~1 wt. ppm, and (ii) characterise the density and binding energy of hydrogen traps. TDS has been useful in HE studies, is complementary to mechanical tests [62], and has been widely used to investigate hydrogen-trap interactions in steels [66-72].

The TDS apparatus used in this study was custom-designed at Griffith University [73] and is designated as TDS-GU, and incorporates improvements on the ultra-high-vacuum (UHV) TDS [64] designed by Smith and Scully [74]. This TDS-GU can accurately characterise desorbed hydrogen at concentrations of $1 \mu\text{g g}^{-1}$ (wt ppm) [73]. The TDS of Smith and Scully was used to investigate hydrogen embrittlement of Al-Li-Cu-Zr alloys, hydrogen trapping in experimental steels [75, 76], and hydrogen trapping and hydrogen embrittlement of ultra-high-strength steels [77-79]. The current work is the first application of this new TDS-GU to understanding hydrogen-steel interactions. In addition, some identical TDS measurements were carried out at Ghent University using a commercial TDS, designated herein as TDS-C, to provide comparative measurements.

The two common methods for hydrogen charging are: (i) electrochemical charging and (ii) gaseous charging. Electrochemical hydrogen charging typically involves the application of a cathodic potential to a specimen, immersed in an acidic or alkaline solution, to liberate hydrogen at the specimen surface. Gaseous hydrogen charging involves exposing a specimen to gas phase hydrogen at a high pressure.

Past studies have related the equivalent gaseous hydrogen pressure or fugacity, f_{H_2} , to the electrochemical charging overpotential, η [80, 81]. Liu et al. [82] found that the relationship between equivalent hydrogen fugacity f_{H_2} and the overpotential η , for low interstitial carbon steel, electrochemically hydrogen charged in 0.1 M NaOH, was given by [82]:

$$f_{H_2} = 15.360 \exp\left(\frac{-\eta F}{3.30RT}\right), \text{ for } |\eta| < 0.35 \text{ V} \quad (1)$$

$$f_{H_2} = 560 \exp\left(\frac{-\eta F}{14.35RT}\right), \text{ for } |\eta| > 0.35 \text{ V} \quad (2)$$

where F is the Faraday constant, R is the gas constant, and T is the absolute temperature. Bockris et al [83] attributed these two different regimes to the two mechanisms governing electrochemical hydrogen evolution: (i) the coupled discharge-recombination mechanism at low overpotential; and (ii) the fast electrochemical discharge at high overpotential.

The present work builds on the study by Liu et al. [48] to understand the influence of hydrogen on 3.5NiCrMoV steel. The specific issues addressed herein are as follows:

1. The characterisation of hydrogen in the 3.5NiCrMoV steel after: (i) cathodic hydrogen charging in two aqueous electrolytes, and (ii) gaseous hydrogen charging,
2. The relationship of the electrochemical charging potential to an equivalent gaseous hydrogen pressure or fugacity,
3. The identification of hydrogen traps in the steel.

2. Experimental methods

2.1 TDS-GU Apparatus

Fig. 1a presents a schematic of the TDS-GU apparatus. A full description is provided in Tapia-Bastidas et al [73]. The TDS-GU apparatus had three main parts: (i) an analysis chamber (AC), (ii) the calibration rig that is used to perform instrument calibration with hydrogen gas, and (iii) the loading chamber (LC). The LC allows a specimen to be introduced into the ultra-high-vacuum of the analysis chamber. The specimen is introduced into the loading chamber, held there until the vacuum has reached a sufficiently low value, and then transferred to the analysis chamber. After the sample has reached ultra-high-vacuum conditions in the AC, it is possible to analyse the gases desorbed from the specimen upon

specimen heating. The specimen is heated via a linear temperature ramp. The desorbed species (such as hydrogen, oxygen, water and carbon dioxide) are continuously analysed and measured by the residual gas analyser (RGA), a type of mass spectrometer.

Quantitative hydrogen calibration used commercial hydrogen standards (purchased from LECO Australia Pty Ltd) (i) developed for the calibration of instruments for measuring the amount of hydrogen by hot extraction, and (ii) factory verified against NIST (National Institute of Standards and Technology) standards. These calibration standards were 4 mm in diam x 8 mm in length, and had a nominal mass of 1 g. They were available with nominal hydrogen contents of $1 \mu\text{g g}^{-1}$ and $5 \mu\text{g g}^{-1}$, which corresponded to actual hydrogen contents of $0.9 \pm 0.4 \mu\text{g g}^{-1}$ and $5.3 \pm 0.4 \mu\text{g g}^{-1}$.

The hydrogen calibration consisted of running a series of TDS-GU evaluations using the commercial calibration standards under the repeatable conditions, as summarized in Table 1. These same TDS-GU test conditions were used for analysing the 3.5NiCrMoV steel specimens.

The appendix contains details of the TDS-GU calibration, the investigation of the influence of adsorbed water, and a discussion of instrument calibration and corrections.

2.2 3.5NiCrMoV steel

The 3.5NiCrMoV steel was a commercial, quenched-and-tempered, martensitic steel, supplied to strength and ductility specifications, by a commercial supplier. Table 2 presents the chemical composition of the steel obtained from two independent measurements carried out by Spectrometer Services Pty Ltd, Coburg North, Vic 3058, and two determinations of mechanical property values [48]. Specimens were discs, 8 mm in diameter x 2.5 mm in thickness, prepared by water jet cutting from a round bar. Each specimen was polished to 1 μm diamond, dried with ethanol, and stored in an argon glove box until needed.

2.3 Electrochemical hydrogen charging

Cathodic hydrogen charging was performed using a three-electrode electrochemical cell. The steel specimen was the working electrode, platinum was the counter electrode, and

Hg/Hg₂SO₄ was the reference electrode. Cathodic hydrogen charging was carried out at 25 ± 2 °C under the following conditions:

- (i) at -1628 mV_{Hg/Hg₂SO₄} (-970 mV_{SHE}), -1728 mV_{Hg/Hg₂SO₄} (-1070 mV_{SHE}), -1828 mV_{Hg/Hg₂SO₄} (-1170 mV_{SHE}), -1928 mV_{Hg/Hg₂SO₄} (-1270 mV_{SHE}), and -2228 mV_{Hg/Hg₂SO₄} (-1570 mV_{SHE}) in 0.1 M NaOH (pH 13), and
- (ii) at -1090 mV_{Hg/Hg₂SO₄} (-432 mV_{SHE}), -1290 mV_{Hg/Hg₂SO₄} (-632 mV_{SHE}), -1390 mV_{Hg/Hg₂SO₄} (-732 mV_{SHE}), -1490 mV_{Hg/Hg₂SO₄} (-832 mV_{SHE}), -1690 mV_{Hg/Hg₂SO₄} (-1032 mV_{SHE}), and -1790 mV_{Hg/Hg₂SO₄} (-1132 mV_{SHE}) in 0.1 M Na₂SO₄ (pH 2, acidified using H₂SO₄).

To ensure complete hydrogen saturation of the steel, the charging duration was 24 hour [82]. All solutions were prepared using analytical reagent grade chemicals and distilled water.

At the end of the charging period, the specimen was removed from the electrolyte, dried with inert gas, and immediately loaded into the TDS-GU apparatus.

2.4 Gaseous hydrogen charging

Gaseous hydrogen charging was performed using a fabricated hydrogen charging apparatus, which comprised a specimen chamber and chamber containing the hydrogen source. The specimen was placed inside the specimen chamber, the specimen chamber was evacuated, flushed with hydrogen, and evacuated using a rotary pump. Hydrogen was introduced into the specimen chamber by heating an attached high-purity metal-hydride hydrogen source (multi-substituted AB₅ intermetallic based on mischmetal) with a laboratory heat gun until the desired hydrogen pressure was reached. Specimens were hydrogen charged at hydrogen pressures of 2, 20, 80, and 200 bar, for a duration of 24 hour. The steel was activated during the first two hours of hydrogen gas charging by heating the pressurized chamber in a vertical tube furnace to 200 °C, after which the furnace was turned off and the chamber was allowed to cool in the furnace to room temperature. At the end of the 24-hour hydrogen-charging period, the specimen was retrieved from the charging chamber and immediately tested in the TDS-GU.

2.5 TDS-GU analysis

Table 1 summarizes the TDS-GU testing conditions used during analysis of the hydrogen charged specimens. The following were carried out after hydrogen charging to minimize the amount of adventitious water on the steel specimen. Firstly, the specimen was handled with a stream of ultra-high-purity (UHP) nitrogen when outside the charging cell to reduce water adsorption from atmosphere. Secondly, the specimen was kept for two hours in the loading chamber prior to loading the specimen into the analysis chamber. Wei and Tsuzaki [84] recommended keeping test specimens in high-vacuum to homogenize surface-water and overcome the possible impedance caused by surface contamination during exposure to ambient atmosphere.

The procedure for specimen loading and TDS-GU analysis was as follows. From a high vacuum state, the loading chamber (LC) was brought to atmospheric pressure. Ultra-high-purity (UHP) nitrogen was injected into the LC chamber to speed up reaching atmospheric pressure, and to minimize water adsorption onto the LC chamber walls. The LC door was opened when atmospheric pressure was reached. The specimen was loaded into the LC. The stream of UHP nitrogen inside the chamber was maintained while the LC door was open to prevent water contamination of the LC. The mounting of the specimen on the specimen holder was also done adjacent to the LC loading door so that the escaping nitrogen gas protected both the specimen and the specimen holder. Once the specimen was loaded into the LC in the specimen holder, the LC door was closed, and the LC chamber was evacuated. High vacuum was typically achieved within 40 minutes. A dwell time of exactly 120 minutes was adopted; i.e. from end of hydrogen charging to specimen loading into the LC to transferring to the analysis chamber (AC), in order to facilitate desorption of all surface contaminants from the specimen surface (particularly adsorbed water), and to ensure uniformity of results between measurements. At the end of the dwell time, the specimen was transferred to the analysis chamber, AC. The AC was stabilised for 12.5 minutes before the main gate valve was throttled to a fixed position of 30% open. There was an additional 2.5 minute stabilisation time prior to commencement of the TDS-GU analysis.

To start the TDS-GU analysis, the furnace was turned on and was set to the desired temperature of 870 °C. The heating occurred at the set temperature ramp of 2 °C min⁻¹. The residual gas analyser (RGA) was simultaneously started to measure the concentrations of the desorbed gases. Once the target temperature was reached, the furnace was turned off. The

specimen was allowed to cool in the AC, and was retrieved after the AC reached room temperature.

2.6 TDS-C measurements

Comparative measurements were carried out on a commercial TDS apparatus at Ghent University, designated as TDS-C using the 3.5NiCrMoV steel discs supplied from the same batch as analysed in the TDS-GU, 8 mm in diam x 2.5 mm in thickness, sent by airmail from Australia to Ghent. These samples were cathodically hydrogen charged (i) as received from Australia, and (ii) after regrinding and repolishing to 1 μm . Cathodic hydrogen charging was for 24 h in 0.1 M NaOH at 25 °C at $-1.6 V_{\text{Hg/Hg}_2\text{SO}_4}$ ($-0.95 V_{\text{SHE}}$), $-1.8 V_{\text{Hg/Hg}_2\text{SO}_4}$ ($-1.15 V_{\text{SHE}}$), and $-2.2 V_{\text{Hg/Hg}_2\text{SO}_4}$ ($-1.55 V_{\text{SHE}}$) in a three electrode cell, with the steel sample the working electrode, a Hg/Hg₂SO₄ reference electrode and a platinum counter electrode. In some cases, 1.0 g L⁻¹ thiourea (a recombination poison) was added to the 0.1 M NaOH solution for cathodic hydrogen charging at $-2.2 V_{\text{Hg/Hg}_2\text{SO}_4}$ ($-1.55 V_{\text{SHE}}$).

The commercial TDS-C was supplied by Bruker. Fig. 1b provides a schematic. This new TDS-C started analysis after ~1 min after the end of charging, because there was no need for a waiting time to reach vacuum in the analysis chamber. A novel technique was elaborated for which an external furnace was used to perform the TDS experiments. As such, vacuum was no longer a requirement, and the TDS measurement could start one minute after hydrogen charging. The hydrogen content was detected by a mass spectrometer, which was under constant vacuum. Calibration was done by a standard gaseous calibration method and using LEco calibration standards as for the TDS-GU. The heating rate used was 2 °C min⁻¹. A thermocouple was placed on the sample to follow the sample temperature.

The hydrogen was detected by a mass spectrometer that measured current (micro ampères) versus cycles. A specifically developed software program calculated, taking into account the calibration, the amount of hydrogen present under the peak. While doing this calculation, the baseline was simultaneously subtracted. To analyze the raw data, these results needed to be converted to wppm/s by integrating the whole peak and taking into account the heating rate. Additionally, the cycles were converted to temperature by the data generated by the thermocouple, which was in contact with the sample.

3. Results

3.1 Electrochemical charging in 0.1 M NaOH

Fig. 2 shows the hydrogen spectra of the 3.5NiCrMoV steel electrochemically hydrogen charged at the stated potentials in 0.1 M NaOH, measured using the TDS-GU. There were significant composite peaks at ~150 °C that correspond to diffusible hydrogen [85], and some small peaks at higher temperatures attributed to adventitious water on the specimen surface. The diffusible hydrogen peak height increased with increasingly negative charging potentials, consistent with higher hydrogen concentrations corresponding to more negative cathodic hydrogen charging potentials. The composite hydrogen peak moved to lower temperatures with increasing peak height, consistent with a constituent peak at the lowest temperature increasing in peak height with increasing hydrogen fugacity.

To allow assessment of the different trapping states for hydrogen corresponding to the measured peaks, deconvolution of the spectra was performed using the ORIGIN 9 software. Each spectrum was fitted to three Gaussians peaks. An iterative trial-and-error process was followed until the numerical fitting converged for the data of Fig. 2, and also the data of Fig. 4, and Fig. 7, to a pre-set chi-square tolerance factor equivalent to 1×10^{-6} .

Fig. 3 shows the spectra was deconvoluted to three hydrogen peaks centred at 114 °C, 160 °C and 210 °C. Each of these desorption peaks was attributed to a characteristic hydrogen trap in the steel. The desorption peak at 114 °C was the most sensitive to the charging potential. The height of this peak increased with increasingly negative applied potential, as expected from the raw data in Fig. 2. The peaks at 160 °C and 210 °C were marginally influenced by the charging potential, although the 210 °C peak slightly decreased at the most negative charging potential.

3.2 Electrochemical charging in 0.1 M Na₂SO₄

Fig. 4 presents the TDS-GU hydrogen desorption spectra of the samples electrochemically charged in 0.1M Na₂SO₄ at the stated charging potentials, measured with the TDS-GU. The Y-axis of Fig. 7 is the same as that of Fig. 2 for easy comparison. The spectra were dominated by the peaks below 300 °C corresponding to diffusible hydrogen, but there were substantial peaks at ~340 °C which were again attributed to adventitious surface adsorbed water. These peaks had peak heights comparable to that in Fig. A3a, which was

attributed completely to adsorbed water. The diffusible hydrogen peak heights increased with increasingly negative charging potentials, similar to the diffusible hydrogen peaks of the steel charged in 0.1 M NaOH

Fig. 5 presents the deconvolution of the diffusible hydrogen spectra. Again, the intensity of the peak at 114 °C increased with increasingly negative potentials, consistent with the steel charged in the 0.1 M NaOH solution. The peak height of the 160 °C peak was constant below -1490 mV_{Hg/HgSO₄}, then decreased at more negative cathodic potential, and was not detected after charging at the most negative potential of -1760 mV_{Hg/HgSO₄}. The peak height of the 210 °C peak was essentially constant at all potentials.

3.3 TDS-C measurements

No hydrogen was detected using the TDS-C at Ghent University for as-received 3.5NiCrMoV steel after cathodic hydrogen charging was for 24 h in 0.1 M NaOH at 25 °C at -1.6 V_{Hg/Hg₂SO₄} (-0.95 V_{SHE}), -1.8 V_{Hg/Hg₂SO₄} (-1.15 V_{SHE}), and -2.2 V_{Hg/Hg₂SO₄} (-1.55 V_{SHE}). These experiments were carried out with the same 3.5NiMoV specimens as tested in the TDS-GU in Australia. The 3.5NiCrMoV specimens were sent from Australia to Ghent by airmail.

Some specimens were polished to 1 µm diamond, subjected to cathodic hydrogen charging, and retested using the TDS-C.

Fig. 6a presents the TDS-C spectra for 3.5NiCrMoV steel, freshly polished to 1 µm diamond, and cathodically hydrogen charged in 0.1 M NaOH at the stated potentials for 24 h. There was significant hydrogen in these specimens as indicated by the broad peak for temperatures between room temperature and 200 °C. The amount of hydrogen increased with increasingly negative cathodic charging potential, and the peak moved to lower temperatures, consistent with the data measured with the TDS-GU, and illustrated in Fig. 2. The amount of hydrogen was similar to that measured using the TDS-GU and listed in Table 3. There were no hydrogen peaks at temperatures above 200 °C, which was consistent with the interpretation that the peaks above 200 °C in Figs. 2, 4 and 7 do not pertain to hydrogen in the specimen.

Fig. 6b presents the TDS-C spectra for 3.5NiCrMoV steel, freshly polished to 1 µm diamond, and cathodically hydrogen charged in 0.1 M NaOH at -2.2 V for 24 h, without and with the presence of 1.0 g L⁻¹ thiourea in the solution. There was significantly more hydrogen

in the specimen charged with thiourea in the solution, as expected, because thiourea is a hydrogen recombination poison, and its presence causes a higher hydrogen uptake into the specimen.

3.4 Gaseous Charging

Fig. 7 presents the typical TDS-GU hydrogen spectra of one series of experiments of the 3.5NiCrMoV steel charged in gaseous hydrogen at hydrogen pressures of 2, 20, 80 and 200 bar. The Y-axis of Fig. 7 is the same as those of Fig. 2 and Fig. 4 for easy comparison. Subsequently, extra measurements were carried out at 2, 20 and 200 bar.

The peak at 340 °C is again attributed to surface-adsorbed water.

Again, analysis is limited to peaks corresponding to diffusible hydrogen that were at temperatures below 300 °C. The intensity of these peaks, and therefore the hydrogen concentration, increased with increasing charging pressure, and the peak position moved to lower temperatures.

The shape of the spectra for the hydrogen gas charged steels was slightly different from the electrochemically hydrogen charged counterparts; indicating the possibility of some trapping centres being inactive.

Fig. 8 shows the deconvoluted hydrogen spectra for the 3.5NiCrMoV steel charged in gaseous hydrogen at different hydrogen pressures. There were only two desorption peaks, at 114 °C and 160 °C, in contrast with the three peaks in the electrochemically charged steels. The intensity of the peak at 114 °C was directly proportional, whilst that at 160 °C was inversely proportional, to the charging pressure.

4. Discussion

4.1 TDS-GU v TDS-C

The TDS-C data indicated that the details of surface preparation had a large influence on the amount of hydrogen absorbed by the specimen from 24 h cathodic charging in 0.1 M NaOH. No hydrogen was absorbed for the as-received specimens, whereas a significant amount of hydrogen was adsorbed for the freshly polished specimens. These data indicate

that the surface oxide that forms on the surface of the 3.5NiCrMoV steel at room temperature was sufficient to prevent hydrogen absorption during 24 h cathodic charging in 0.1 M NaOH at $-2.2 \text{ V}_{\text{Hg}/\text{Hg}_2\text{SO}_4}$. Examination of the E-pH diagram [86] for Fe indicates that the evolution of hydrogen reduces the surface film on Fe in equilibrium. However, the above data indicates that this reduction is a slow process. This is consistent with the observation of Liu and Atrens [87], using unstressed permeation experiments, that steady state surface conditions were established on the surface of 3.5NiCrMoV steel after 19 h of cathodic charging in 0.1 M NaOH. It is also consistent with the observations of Pérez Escobar et al. [71] that more hydrogen was adsorbed by a polished sample compared with a ground sample.

Given the significant influence of specimen preparation, the data measured with the TDS-C were in good agreement with the data measured using the TDS-GU in regard to the amount of hydrogen absorbed by the 3.5NiCrMoV steels in the hydrogen peaks in the temperature range from room temperature to 200 °C, as is clear from a comparison of Fig. 6, Fig. 2, and Table 3.

There were no hydrogen peaks above 200 °C in the TDS-C spectra, Fig. 6, confirming the interpretation that the peaks above 200 °C in the TDS-GU spectra, Figs. 2, 4 and 7, were not associated with hydrogen in the specimen, but were associated with the decomposition of chemically bound water on the specimen surface, and that these “water” peaks were detected by the TDS-GU because of its sensitivity.

The TDS peaks above 200 °C measured using the TDS-GU were thus attributed to hydrogen that arose from the catalytic decomposition at the specimen surface during the TDS measurements. This catalytic decomposition produced hydrogen evidently from hydrogen-containing compounds on the specimen surface. These hydrogen-containing compounds are thought to be both adsorbed water (H_2O) as well as oxy-hydroxides, and possibly hydrated sulphates. These compounds can be the result of the hydrogen charging conditions, solution contact after the end of electrochemical hydrogen charging, and water adsorbed onto the specimen surface between the end of hydrogen charging and the commencement of TDS analysis. A comparison of Figs. 4, 2 and 7 indicate that the peak heights were largest after electrochemical charging in 0.1M Na_2SO_4 . This suggests that this electrochemical charging condition produces the most hydrogen-containing surface species.

The TDS-GU did measure these peaks at temperatures above 200 °C, and these peaks do relate to hydrogen, as the TDS-GU detector measures hydrogen. The TDS-C does detect

hydrogen associated with the specimen at temperatures above 200 °C, and such measurements have been published. However, it was observed experimentally, that the TDS-C did not detect any peak at temperatures above 200 °C after electrochemical hydrogen charging under conditions similar to those that had produced the hydrogen peaks in the TDS-GU. There are two possible reasons. These hydrogen peaks are thus attributed to the catalytic decomposition of hydrogen containing compounds at the specimen surface (i.e. at the surface of the steel) in the ultra-high vacuum of the TDS-GU to produce hydrogen. It is possible that this catalytic decomposition does not occur on the specimen surface in the carrier gas of the TDS-C. It is also possible that the sensitivity of the TDS-C is not sufficient in this temperature range to detect these peaks.

4.2 Hydrogen Loss

Egress of diffusible hydrogen starts at the end of the charging [63]. This highlights the desirability to immediately analyse hydrogen charged specimens to minimize hydrogen loss. However, the current TDS-GU procedure required a dwell-time of 120 min in the loading chamber (LC) to minimize the effect of adventitious water adsorbed by the steel, and a 15 min stabilization period to normalize the UHV in the analysis chamber, prior to TDS-GU measurements. Clearly, it was desirable to quantify the amount of hydrogen lost during this period, as previously identified [63].

The following mathematical model was developed to estimate the amount of effused hydrogen in the steels prior to TDS-GU analysis. A thin plate of thickness, L , with a uniform initial hydrogen concentration of C_0 , with hydrogen outgassing occurring from both sides has the following initial and boundary conditions:

$$C = C_0, 0 < x < L, t = 0 \quad (3)$$

$$C = 0, x = 0, L \text{ (surface)}, t > 0 \quad (4)$$

The solution to Fick's second law is [88]:

$$\frac{C}{C_0} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \left[(2n+1) \pi \frac{x}{L} \right] \exp \left[- \frac{(2n+1)^2 \pi^2 D t}{L^2} \right] \quad (5)$$

where D is the diffusion coefficient of hydrogen in the steel, x is the distance measured from the surface to a point along the thickness of the specimen. This equation provides the value of

the normalised concentration, C/C_0 after any elapsed time, t , which when integrated yields the amount of hydrogen remaining in the steel.

Fig. 9 plots the fraction of hydrogen remaining in a uniform flat specimen as a function of time, thickness and hydrogen diffusion coefficient, D . Two thickness values were evaluated, i.e. 2.6 mm and 0.8 mm. D values ranged from $3.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ to $1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. These curves provide the fraction of hydrogen remaining in a charged sample at a particular time after charging and for the specified diffusion coefficient. The model predicts that after 135 min, the remaining hydrogen is equal to 0.84 and 0.50 of the initial concentration for, $D = 3.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and for a specimen of thickness $L = 2.6 \text{ mm}$ and $L = 0.8 \text{ mm}$, respectively; while it is equal to 0.71 and 0.16 for hydrogen egress for $D = 1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for a specimen of thickness $L = 2.6 \text{ mm}$ and $L = 0.8 \text{ mm}$, respectively.

The analysis leading to Fig. 9 assumes that D is constant with time. However, the permeation experiments by Liu et al. [87] on 3.5NiCrMoV steel indicated that D was somewhat influenced by traps. The effective D value, D_{eff} , changed. The hydrogen effusion was more rapid in the first few minutes, with a higher D_{eff} value. At longer times, trap effects dominated, hydrogen diffusion slowed, and the D_{eff} value was lower. This was the same steel as used in this research.

Fig. 10 provides composite hydrogen egress curves, using the D_{eff} values obtained by Liu et al. and applying these to two time regimes: i.e. $D_{\text{eff}} = 1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the first 5 min and $D_{\text{eff}} = 3.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ after 5 min. The composite curve was used to estimate the amount of effused hydrogen during the pre-analysis period. Fig. 10 shows that the fraction of hydrogen remaining in the specimen after 135 min was equal to 0.83 and 0.46 for a specimen of thickness of $L = 2.6 \text{ mm}$ and $L = 0.8 \text{ mm}$, respectively. This implies that for a 2.6 mm thick specimen, 17% of the hydrogen was lost. Such an amount represents a substantial fraction of the initial hydrogen in the specimen. The measured amount of hydrogen should be corrected by this procedure to give the total amount of hydrogen in the specimens at the end of hydrogen charging.

4.3 Total Hydrogen Concentration

The amount of diffusible hydrogen desorbed from the hydrogen charged specimen was obtained by performing a numerical integration (using ORIGIN 9) of the area below the desorption peaks at temperatures less than 300 °C. Table 3 summarizes the hydrogen

concentrations for the specimens charged in the 0.1 M NaOH and 0.1 M Na₂SO₄ solutions. Two hydrogen concentration values are presented in columns 4 and 5: (i) ‘as measured’, obtained via peak area integration of the whole hydrogen TDS-GU spectra and applying the corrected calibration curve (Fig. A2) and (ii) ‘as measured after H loss correction’ peak, calculated by adding the estimated amount of hydrogen lost during the 135 min pre-analysis dwell time to the hydrogen concentration corresponding to the 114 °C, then adding the hydrogen concentration corresponding to the two other peaks; i.e. at 160 °C and 210 °C.

The total hydrogen concentration is given by the sum of the hydrogen associated with the peak at 114 °C plus the hydrogen associated with the peak at 160 °C plus the hydrogen associated with the peak at 210 °C. The hydrogen associated with the peak at 114 °C represents hydrogen so weakly trapped that it diffuses readily out of the specimen, thus the amount of hydrogen originally in the specimen was higher than that associated with the measured peak area, so this must be corrected as described. In contrast the other two peaks represent hydrogen much more deeply trapped, so that essentially no hydrogen was lost, and no correction was needed. Thus the total hydrogen originally in the specimen equals (the amount originally in the specimen associated with the 114 °C peak given by the measured 114 °C peak corrected for hydrogen lost) plus (the amount originally in the specimen associated with the 160 °C peak given by the measured 160 °C peak which needs no correction for hydrogen lost) plus (the amount originally in the specimen associated with the 210 °C peak given by the measured 210 °C peak which needs no correction for hydrogen lost).

Fig. 11a presents a plot of the corrected hydrogen concentration for the electrochemically hydrogen charged specimens in the two electrolytes at different applied overpotentials, η . The use of η , instead of the applied potential, provides an appropriate basis for comparing the results for the two different solutions. These results indicated that: (i) the hydrogen content of the steel increased with increasing charging overpotential; and (ii) hydrogen charging in the 0.1 M Na₂SO₄ electrolyte (0.204 to 1.472 $\mu\text{g g}^{-1}$) produced higher hydrogen concentrations in the steels than hydrogen charging in the 0.1 M NaOH solution (0.197 to 0.585 $\mu\text{g g}^{-1}$). Fig. 11a presents lines drawn to show the trend in the measured values. Both curves had a knee in the trend. In the 0.1 M NaOH, the knee occurred at 0.55 V; whilst in the 0.1 M Na₂SO₄, this occurred at 0.62 V.

Fig. 11b compares the values of hydrogen concentration evaluated in the present study with the hydrogen concentration values evaluated by Liu et al. [87], from hydrogen permeation experiments [89]: (i) calculated directly from the experimental data, and (ii) as evaluated using the Oriani-Dong trapping model. The hydrogen measurements in the current study were typically somewhat higher than those measured by Liu et al. The difference between the values was highest at low overpotentials, decreased at more negative overpotentials, and disappeared for overpotentials above 0.7 V.

Deconvolution of the diffusible hydrogen spectra indicated that only the 114 °C peak increased directly proportional to the applied overpotential. It is reasonable to assume that this trap was responsible for the diffusible hydrogen that effused at room temperature from the steel, because it was the weakest due to having the lowest peak temperature. Conversely, the traps at the higher temperatures (i.e. 160 °C and 210 °C) were associated with more-highly trapped hydrogen. Measurement of the area under the 114 °C peak gave the concentration of hydrogen associated with this trap.

Table 3 includes the as measured and corrected hydrogen concentration corresponding to the 114 °C peak for the specimens charged in 0.1 M NaOH and 0.1 M Na₂SO₄ solutions. Fig. 11c shows a plot of the diffusible hydrogen concentration, as measured using only the 114 °C peak and corrected for hydrogen egress, as a function of the overpotential in the two charging electrolytes. The hydrogen concentration of the steels charged in the acidic electrolyte was higher than those in the steel charged in the alkaline solution. There was no ‘knee’ in the data. The trend was defined by a single line.

Table 4 presents the as-measured and corrected hydrogen concentrations of the hydrogen gas charged steels calculated using (i) the whole spectra and (ii) 114°C peak. There was a direct relationship between the charging pressure and the calculated hydrogen concentration. The measured values were all less than 0.9 µg g⁻¹ (0.568 to 0.889 µg g⁻¹), which were generally lower than those measured for the electrochemically charged steels in 0.1 M NaOH or 0.1 M Na₂SO₄.

Sieverts’ law indicates that the concentration of the dissolved hydrogen in a steel, C_H , is proportional to the partial pressure, often expressed as fugacity, f_{H_2} , [90]:

$$C_H = S\sqrt{f_{H_2}} \quad (6)$$

where S is the solubility constant, which is dependent on temperature and the type of steel. Fig. 12 presents a plot of all the corrected TDS-GU-measured hydrogen concentration values against the square root of hydrogen charging pressure, $p^{1/2}$. The plot shows linearity consistent with Sieverts' law. Section 4.7 develops a two-site model for Sieverts' Law that explains the positive Y-intercept as the density of already filled hydrogen traps at room temperature.

4.4 Hydrogen fugacity

The information from the TDS-GU measurements can establish the relationship of charging potential to hydrogen fugacity. This begins with the regression line obtained from the plot of hydrogen concentration vs $p^{1/2}$ (i.e. Fig. 12). This line establishes an empirical relationship between hydrogen concentration and hydrogen charging pressure. Therefore, the measured hydrogen concentrations of the electrochemically charged specimens may be superimposed on this line to determine the equivalent charging pressure. Fig. 13 shows the resulting curve. Fig. 13 used the regression line from Fig. 12, which used the corrected total hydrogen concentration from the integration of the TDS-GU spectra. Fig. 13 indicates that the equivalent charging pressures during electrochemical charging were higher than those present during gaseous charging. Section 4.7 provides a discussion of how this extrapolation is supported by the filling of the hydrogen traps as revealed by the TDS data.

The final step is to match the derived equivalent pressures, from Fig. 13, to the corresponding charging potential. Fig. 14a presents the equivalent fugacity plotted against the charging overpotential, corresponding to the hydrogen concentrations derived from the whole TDS-GU hydrogen spectra.

Fig. 14b compares the current results with past studies that similarly determined the equivalent fugacity during electrochemical charging for a low interstitial steel (i.e. pure Fe) by Liu et al. [82] and pure Armco iron from the data of Bockris et al. [91] as analysed by Liu et al. The values obtained from the data of Bockris et al. were the lowest among the three groups of measurements. The current study and Liu et al had contrasting results. We measured hydrogen concentrations for the 3.5NiCrMoV steel higher than for the low interstitial steel charged in 0.1 M Na₂SO₄; whilst Liu et al. measured hydrogen concentrations for the low interstitial higher than for the 3.5NiCrMoV steel charged in 0.1 M NaOH. This clearly indicates that details of the hydrogen evolution reaction are different on the surfaces of the different steels, a not unexpected result.

The National Institute of Standards and Technology (NIST) has produced an extensive data base regarding the equations of state (EOS) for hydrogen, including the isothermal density of hydrogen, $\rho(p)$, for pressures up to 20 kbar. Using this NIST data, the hydrogen fugacity, f , can be related to the hydrogen pressure, p , by the following expression:

$$f = f^o \exp \left(\frac{1}{RT} \int_{p^o}^p \frac{1}{\rho(p)} dp \right) \quad (7)$$

where f^o is the fugacity at the standard state, p^o is the pressure at the same standard state, e.g. $f^o = 1$ bar when $p^o = 1$ bar; R is the gas constant, T is the absolute temperature; and the integration is carried out from the standard pressure p^o up to the pressure of interest p .

Sezgin et al. [92, 93] carried out this integration, and relate the hydrogen fugacity, f , to the hydrogen pressure, p , by the following expression:

$$f(p) = p \exp \left(\frac{pb^o}{RT} - \alpha \frac{p^2}{RT} \right) \quad (8)$$

where $b^o = 1.4598 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, $\alpha = 1.955 \times 10^{-15} \text{ m}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$, R is the gas constant = 8.314, T is the temperature in K, and f and p are expressed in Pa. This equation is valid for temperatures above 200 K and for the following hydrogen pressure range: $1 \text{ bar} < p < 20\,000 \text{ bar}$.

Fig. 15 provides a plot of Eq. (8) as the normalised hydrogen fugacity, that is the quantity (hydrogen fugacity/hydrogen pressure), plotted against the hydrogen pressure. Eq. (8) allows evaluation of values of hydrogen fugacity, f , for various values of the hydrogen pressure, p . Eq. (8) should be used rather than Fig. 15, because it is more precise.

The right hand Y-axis of Figs. 14(a) and 14(b) present the values of hydrogen pressures corresponding to those values of the hydrogen fugacity on the left hand scale, using Eq. (8).

4.5 Electrochemical charging

The relevant peaks in the TDS-GU spectra of the 3.5NiCrMoV steel after electrochemical hydrogen charging were present at temperatures less than 300 °C. While there is paucity in published TDS-GU spectra for 3.5NiCrMoV with which to compare the current results, the spectra from steels having the same martensitic microstructure may be relevant. Sun et al. [94] studied hydrogen trapping in 0Cr16Ni5Mo martensitic steel. At a

heating rate similar to that used in this study, they also measured hydrogen peaks only below 300 °C, and at peak temperatures (e.g. 172 °C and 225 °C) similar to those measured in the current study. Despite an obvious difference in alloying content, the fact that similar TDS-GU spectra were measured in that steel could indicate the strong influence of microstructure on hydrogen trapping. That is, the microstructure is more important than the composition.

The nature of the trap site (e.g. dislocation, grain boundary, lath boundary, etc.) in the steel is not determinable in the present work, since it requires the measurement of trap activation energies, which requires performing measurements at multiple heating rates. On the other hand, Sun et al. [94] measured activation energies less than 22 kJ mol⁻¹ in martensitic 0Cr16Ni5Mo, indicating that the principal traps were dislocations, crystal lattice sites and interfaces. It is also likely that these traps were similarly present in the 3.5NiCrMoV steel.

Table 3 and Fig. 11 confirm that the hydrogen concentration of the steels increased with increasingly negative charging overpotential in both 0.1 M NaOH and 0.1 M Na₂SO₄ electrolytes. This is consistent with expectations. Previous studies have confirmed the direct relationship of hydrogen fugacity to charging overpotential, and consequently to hydrogen concentration [81, 82].

The relatively higher hydrogen uptake of the steels charged in the acidic Na₂SO₄ solution is attributed to the details of the hydrogen evolution reaction in this electrolyte, but the study of these details is outside the scope of this study.

The deconvoluted spectra in Fig. 3 and 5 revealed the hydrogen traps that were active during electrochemical charging. There were three distinct trap sites for charging in both electrolytes. The difference between the two methods was in the way these trap sites filled with changes in charging potential. The peak at 114 °C increased with increasingly negative potentials, regardless of the charging electrolyte. This indicated that this trapping mechanism was insensitive to the charging electrolyte. The behaviour of the other peaks (at 160 °C and 210 °C) appeared to be somewhat affected by the type of electrolyte, but this could be related to the quality of the data.

Fig. 11b indicated that there was reasonable agreement between the total hydrogen for the specimens charged in 0.1 M NaOH measured in this work with TDS-GU with that measured by Liu et al.[87] measured using hydrogen permeation.

4.6 Gaseous charging

Table 4 and Fig. 12 indicated that hydrogen concentration, C_H , in the 3.5NiCrMoV steel increased with increasing hydrogen-charging pressure. The linear relationship of C_H versus $p^{1/2}$ indicates that hydrogen dissolution in the steel during gaseous charging was consistent with Sieverts' law.

A comparison of the de-convoluted peaks in Fig. 8 and 3 revealed that only two hydrogen trap sites (corresponding to the TDS-GU peaks at 114 and 160 °C) were active during gas phase charging, in contrast with the three sites (corresponding to the TDS-GU peaks at 114, 160, 210 °C) present during electrochemical charging. Since the traps occurred at common temperatures, this means that the same type of hydrogen traps operated for both charging techniques. If the desorption temperature is directly related to trap activation energy value, the results suggest that gas charging could only activate lower energy traps; conversely, electrochemical charging could activate higher energy traps. This is consistent with the hydrogen fugacity associated with the two types of hydrogen charging.

The ability for hydrogen to occupy high-energy traps in the steel would be related to the chemical potential of the hydrogen during charging as the hydrogen entered the steel lattice. This implies that the hydrogen formed during electrochemical charging had a higher chemical potential than the hydrogen present during gaseous charging. This is consistent with the higher equivalent fugacity/pressures during the electrochemical charging than in gaseous charging, as indicated by Fig. 13.

4.7 Two-site model of Sieverts' Law

Sieverts' Law may be derived by equating the chemical potentials of hydrogen in the gaseous and solid phases. Fukai [95] provides a summary of the relevant statistical mechanics and references. The chemical potential of gaseous hydrogen, of pressure (or fugacity) p , is approximately:

$$\mu_{H_2} = \varepsilon_b + k_B T \ln \left(\frac{p}{p_0} \right) \quad (9)$$

where the ideal gas law has been assumed and $\varepsilon_b = -4.519$ eV per hydrogen atom is the electronic energy relative to dissociated atoms. The thermodynamic reference pressure (fugacity) is:

$$p_0 = \frac{I}{h^5} \left(\frac{m_{H_2}}{2\pi} \right)^{3/2} (k_B T)^{7/2} \quad (10)$$

where m_{H_2} is the molecular mass, h is the reduced Planck constant $\left(\frac{h}{2\pi} \right)$, and I_{H_2} is the moment of inertia of the diatomic hydrogen molecule [96]. With T in kelvin and p in bar, then:

$$p_0 \approx \left(\frac{T}{9.1312} \right)^{7/2} \quad (11)$$

with a value of 2.033×10^5 bar at 300 K.

To calculate the chemical potential of hydrogen in the steel, suppose that N_H hydrogen atoms are distributed among N_s sites of which N_t are trap sites with site energy, $\varepsilon_t = \varepsilon_s - \Delta\varepsilon$, compared to the energy ε_s of the undisturbed sites. The undisturbed or normal interstitial sites are those occurring in the perfect crystal lattice. In simple BCC metals, hydrogen normally occupies tetrahedral interstices (two per cube face). Defining $\Delta\varepsilon > 0$, the trap site has the lower energy, with relative binding energy $\Delta\varepsilon$, and is preferentially occupied. The following treatment of the two-site problem broadly follows Fukai [95], but an error has been corrected concerning the chemical potential of hydrogen in the metal when the trap sites have been filled. Cannelli et al. [97] provides a more general treatment. Hydrogen-hydrogen (H-H) interactions are not included because the hydrogen concentrations of interest are in the ppm range.

The hydrogen atoms are indistinguishable. It is assumed that only one hydrogen atom may occupy a given site. Therefore Fermi-Dirac statistics are used to distribute the hydrogen atoms over the two types of site:

$$\frac{N_s - N_t}{e^{(\varepsilon_s - \mu)/kT} + 1} + \frac{N_t}{e^{(\varepsilon_s - \Delta\varepsilon - \mu)/kT} + 1} = N_H \quad (12)$$

where μ is the chemical potential of hydrogen on a per-atom basis. The chemical potential is the same for all hydrogen atoms in equilibrium and is set by the external hydrogen pressure (fugacity), thus determining the site occupancies via Eq. (12). Introducing $x = N_H/N_s$ and, $r = N_t/N_s$, Eq. (12) becomes

$$\frac{1-r}{e^{(\varepsilon_s-\mu)/kT}+1} + \frac{r}{e^{(\varepsilon_s-\mu)/kT} \cdot e^{-\Delta\varepsilon/kT}+1} = x \quad (13)$$

Eq. (13) may be solved exactly for the chemical potential of H in the metal. Inspection of the terms allows the most important features of the μ - x relationship to be uncovered.

At the lowest applied pressures, the trap sites fill preferentially, so the first term in Eq. (13) may be neglected, yielding

$$\mu = \varepsilon_s - \Delta\varepsilon + k_B T \log\left(\frac{x}{r-x}\right) \quad (14)$$

which, when equated to the gaseous hydrogen chemical potential in Eq. (9), exhibits Sieverts'-Law behaviour below the maximum possible (trapped) hydrogen concentration r :

$$x \approx p_0^{-\frac{1}{2}} \exp\left(\frac{\varepsilon_B - \varepsilon_s + \Delta\varepsilon}{2k_B T}\right) p^{\frac{1}{2}} \quad (x = r) \quad (15)$$

The terms multiplying $p^{1/2}$ in Eq. (15) correspond to the Sieverts' constant. The value of $\varepsilon_s - \Delta\varepsilon$ may be calculated from experimental isotherm data.

When the pressure increases sufficiently that the trap sites are filled, the second term in Eq. (13) approaches r , yielding for the chemical potential of hydrogen in the metal

$$\mu = \varepsilon_s + k_B T \log\left(\frac{x-r}{(1-r)-(x-r)}\right) \quad (16)$$

which leads to Sieverts'-Law behaviour when the hydrogen concentration is measured with respect to the trap concentration:

$$x \approx r + p_0^{-\frac{1}{2}} \exp\left(\frac{\varepsilon_B - \varepsilon_s}{2k_B T}\right) p^{\frac{1}{2}} \quad (r < x = 1) \quad (17)$$

Therefore a finite intercept on the concentration axis of a $\sqrt{p}$ versus x graph should occur at $x = r$, permitting a direct measurement of the trap density. Again, the terms multiplying $p^{1/2}$ in Eq. (17) correspond to the Sieverts' constant. The value of ε_s can be calculated from experimental isotherm data. Given data in a range of concentrations encompassing the regimes described by Eqs. (15) and (17) a value for $\Delta\varepsilon$ can be obtained.

Eq. (12) can be extended to include further sites with different site energies. If the site energies are sufficiently different, Sieverts' Law behaviour is expected in each concentration range in which a particular site is filling, with r in Eq. (17) representing the total amount of trapped hydrogen in sites with lower energy.

4.8 Analysis of Fig. 13

The TDS analysis in Figs. 3, 5 and 8 indicated that there were three hydrogen traps active in the 3.5NiCrMoV steel. These were the hydrogen traps associated with the TDS peaks at 114 °C, 160 °C, and 210 °C. Furthermore, increasing hydrogen fugacity caused (i) the filling of the traps associated with the 114 °C TDS peak, for both gaseous hydrogen charging and electrolytic charging, and (ii) the traps associated with the 160 °C and 210 °C TDS peaks were full.

Thus, Fig. 13 evidently corresponds to the situation modelled by Eq. (17), with the density of trap sites measured by the intercept on the concentration axis, $0.53 \mu\text{g g}^{-1}$, corresponding to a density of already filled hydrogen traps, $r = 30 \text{ ppm}$ in atom terms. The TDS data indicates that these are the traps associated with the 160 °C and 210 °C TDS peaks. However, because there are no data available at hydrogen pressures below 1 bar, the number of types of trap site contributing to r is unknown from the Sieverts' analysis.

The Sieverts' constant from Fig. 13 is $K = 0.0272 \mu\text{g g}^{-1} \text{bar}^{-1/2} \equiv 1.511 \times 10^{-6} \text{bar}^{-1/2}$ in molar terms, and from Eq. (17), $\varepsilon_s = \frac{\varepsilon_b}{2} - \ln(Kp_0^{1/2}) = -2.07 \text{ eV}$ for the traps associated with the 114 °C TDS peak. Comparing this value to that for the much better-known Pd-H₂ system, for which $\varepsilon_s = -2.35 \text{ eV}$ [98], the value obtained here is reasonable for an interstitial solid solution that desorbs just above room temperature from reversible traps. Thus, the undisturbed sites may be confidently identified with the diffusible hydrogen TDS peak centred at 114 °C, and the peaks at higher temperatures with stronger traps. This interpretation is supported by Fig. 8, in which the lower-temperature peak grows with increasing charging pressure and is mainly responsible for the Sieverts' Law behaviour shown in Fig. 13.

Thus, the interpretation of the equivalent charging pressure from Fig. 13 for the electrochemical charging is strongly supported by this analysis, because the filling of the 114 °C peak is the main cause of the Sieverts' behavior over the whole range of Fig. 13, for both gas phase charging and electrochemical gas phase charging.

There is nevertheless, the interpretation of the higher-temperature peak at 210 °C in the TDS spectra after electrochemical charging. This TDS peak corresponds to a deeper trap,

thus it would be expected that this trap would be filled first, before filling of the traps with lower energy. Thus, the reason for that not being accessed by the gas-phase charging is unclear. It is possibly related to kinetics (diffusion pathways), since the free energy available in the electrochemical case is much higher, due to the higher hydrogen fugacity. It is also possible that this trap had a high activation energy, which would explain why it was not filled by lower-fugacity gas charging.

4.9 Equivalent fugacity

An aim of this study was to determine the relationship of hydrogen fugacity to charging potential during electrochemical charging. These relationships are presented in Fig. 14a. These relationships can be used to predict hydrogen uptake, and hydrogen embrittlement, if data correlating hydrogen concentration to mechanical behaviour is available, for the 3.5NiCrMoV in applications that expose the steel to high-pressure hydrogen. This indicates that this aim of this study has been achieved.

Fig. 14b indicates that the hydrogen fugacity–overpotential relationships for 3.5NiCrMoV steel were somewhat different to those for the low interstitial steel measured by Liu et al [82]. This difference was attributed to differences in the details of the hydrogen evolution reaction of the surfaces of these steels. This indicates that there is some appreciation that the hydrogen charging behaviour depends on the steel being hydrogen charged.

5. Conclusions

A newly-designed, high-sensitivity TDS-GU was used to measure the amount of hydrogen in 3.5NiCrMoV steel after (i) electrochemical charging in 0.1 M NaOH and 0.1 M Na₂SO₄, and (ii) hydrogen charging in high pressure hydrogen.

1. The hydrogen concentration in the steel increased with (i) increasingly negative charging potentials and (ii) increasing hydrogen gas pressure. This increase in hydrogen concentration was due to an increase in the hydrogen fugacity.
2. The equivalent hydrogen fugacity versus charging over-potential was derived for 3.5NiCrMoV steel charged in the two different electrolytes.

3. There was a difference in the diffusible hydrogen traps activated during electrochemical and gas phase charging, attributed to the difference in the hydrogen fugacity.
4. A two-site model for Sieverts' Law explained the positive Y-intercept as the density of already filled hydrogen traps at room temperature.
5. The manner of filling of the lower energy trap sites as shown by TDS underpins the extrapolation of the Sieverts' Law line from the gas phase charging data to the electrochemical hydrogen charging data.

Appendix

A.1 TDS-GU calibration

Fig. A1 shows typical TDS-GU spectra obtained from the TDS-GU analysis of the two calibration standards. Fig. A2 shows the calibration curve obtained using (i) a nominal $1 \mu\text{g g}^{-1}$ standards, (ii) two nominal $1 \mu\text{g g}^{-1}$ standards, (iii) a nominal $5 \mu\text{g g}^{-1}$ standards, and (iv) previously hydrogen degassed standards (that therefore contained no hydrogen) that had been exposed for some time to the laboratory atmosphere. The error bars indicate the statistical error in the measured hydrogen content of the standards.

The results showed good linearity within the range of the certified values of the standards; i.e. from $0.9 \mu\text{g g}^{-1}$ to $5.3 \mu\text{g g}^{-1}$. The obtained linear relationship between the hydrogen content and the integrated peak area was expected to pass through the origin. However, there was a positive Y-intercept attributed to hydrogen from the decomposition of water adsorbed onto the surface of the hydrogen standards, as summarised below, and discussed in more detail in Tapia-Bastidas et al. [73]. This interpretation is supported by the measurements of standard specimens containing no hydrogen, after having been degassed in previous TDS-GU experiments, and having been exposed to the laboratory atmosphere. These measurements indicated hydrogen concentrations consistent with the Y-intercept of the line extrapolated from the certified hydrogen concentration of the commercial Leco hydrogen standards.

To evaluate the actual hydrogen desorbed from a specimen, the calibration line needed to be corrected to offset the contribution from this adsorbed water. The corrected calibration line was obtained by drawing a parallel line that crossed the origin, as shown in

Fig. A2. This line was used to evaluate the hydrogen concentration values in all the tests described herein.

A.2 Surface-adsorbed water

Despite water adsorption on solid surfaces being well known [99], it has been common practice [69, 79, 100, 101] to load the sample for TDS examination immediately after electrochemical charging. A film of water on the specimen is to be expected.

The following experiments examined the contribution of the adventitious water on the specimen surface to the hydrogen spectrum. Fig. A3 presents the TDS-GU spectra, measured with a ramp rate at $2\text{ }^{\circ}\text{C min}^{-1}$, for a $5\text{ }\mu\text{g g}^{-1}$ LECO standard calibration pin for the following conditions: (i) as-received (A, squares), (ii) tested pin re-tested without exposure to the atmosphere (AO, triangles), (iii) tested pin re-tested after 1 min exposure to the atmosphere (A1, circles), (iv) tested pin re-tested after exposure to air for seven hours (A2, diamonds). Fig. A3a presents the hydrogen spectra. Fig. A3b presents the corresponding water spectra.

Fig. A3a shows that the hydrogen spectrum of the as-received $5\text{ }\mu\text{g g}^{-1}$ LECO pin (A, squares) included a shoulder in the region around $340\text{ }^{\circ}\text{C}$. This corresponds to a peak in the water signal, Fig. A3b. This extra hydrogen contribution is attributed to the hydrogen produced by the decomposition of water adsorbed on the specimen. This water was expected to be completely desorbed after a TDS-GU analysis.

The next spectra (AO, triangles) was for the same pin, but without unloading the sample from the apparatus; and therefore without exposure to the atmosphere. The pin was expected to be completely desorbed of hydrogen and water, and indeed, the spectra (triangles, sample AO) show the absence of any peaks corresponding to hydrogen and water. The obtained spectra may be considered as a true instrumental background, with the rise at the highest temperature probably due to hydrogen desorbed from the quartz furnace tube.

The next spectra (A1, circles) involved the pin removed from the TDS-GU, exposed to the laboratory atmosphere for 1 minute, and retested. Fig. A3b indicates a substantial increase in the water spectra, while the hydrogen spectra were just marginally higher, in specimen A1 (circles) relative to the AO spectra (triangles). The amount of water desorbed from A1 (triangles) was smaller ($\sim 40\%$) than that desorbed from the as-received pin (A, squares).

Finally, the same pin was exposed to laboratory atmosphere for 7 h and then re-tested (A2, diamonds), while the sample stage was kept under UHV condition. The resulting spectra of A2 (diamonds) showed that there was a considerable hydrogen spectra, which could be completely attributed to adsorbed water, since the specimen contained no hydrogen. Furthermore, the water signal was quite comparable to that of the fresh pin (A, squares).

These results indicate the ease with which water adsorbs to the specimen surface and provides a considerable spurious hydrogen TDS-GU spectra at ~ 300 °C. Therefore the procedure adopted for TDS-GU measurements aimed to minimize the effect of water on the experimental results.

A.3 Calibration and corrections

The TDS-GU measurements required: (i) a proper calibration; (ii) consideration of the hydrogen from the adventitious water adsorbed on the specimen surface; and (iii) accounting for hydrogen lost between the end of hydrogen charging and the start of TDS-GU analysis.

The calibration of the TDS-GU ensured accurate results within a hydrogen concentration range of 0 to $5.3 \mu\text{g g}^{-1}$. This range is suitable for the current work.

The experiments to understand the effect of hydrogen from the adventitious water adsorbed on the surface of the test specimens lead to the following conclusions. Firstly, the UHV environment of the TDS-GU analysis chamber did not contribute to the water signal. This would be expected and is necessary to ensure that the TDS-GU yields reliable data. Secondly, the water contribution arose from exposure of the test specimens to the laboratory atmosphere. Thirdly, even brief exposures to the laboratory atmosphere lead to water contamination, and are enough to affect the resulting TDS-GU spectra. These conclusions highlight the necessity of minimizing contact between specimen and the atmosphere to minimize the size of the water peak. This statement similarly applies to the sample stage and holder. Some of the measures to control water adsorption included: (i) keeping a protective shroud of UHP nitrogen on the specimen during handling outside of the loading chamber; (ii) keeping the specimen holder in high vacuum at all times and minimizing unnecessary retrievals; and (iii) minimizing the process time between the charging/cleaning stage to the TDS-GU loading stage, (iv) a 120 min dwell-time in the loading chamber.

The current results lead to conclusions similar to those by Silvestri et al. [102] in their TDS-GU study of iridium mass standards. They found that water constituted the major component of the spectra obtained after the samples were cleaned following the recommended procedure [103] and then exposed to the laboratory atmosphere. Furthermore, they observed that the amount of adsorbed water increased with increasing exposure time.

The third important correction was to account for the amount of desorbed hydrogen between the end of hydrogen charging and the start of TDS-GU analysis. The diffusion models proved that a considerable amount of hydrogen was indeed lost during the pre-analysis stage. Depending on the hydrogen diffusion coefficient, specimen thickness, and dwell times, this loss could range from 10% to up to 40% of the total hydrogen in the specimen.

There is an inherent conflict between (i) the requirement to increase the dwell time of the specimen in the vacuum of the TDS-GU to decrease the amount of adventitious water adsorbed on the surface of the test specimens, and (ii) this increased dwell time causing an increase loss of hydrogen from the specimen by diffusion. This conflict has not been addressed herein.

There is also the issue that the present configuration of the TDS-GU is such that detection of hydrogen peaks at temperatures above about 250 °C may be problematical, because of the water peaks. This was not an issue in the present study because the measurements using the TDS-C showed that there were no hydrogen peaks in this temperature range.

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Fig. 1a. Schematic of the thermal desorption spectroscopy (TDS-GU) apparatus. The TDS apparatus allows measurement of the amount of hydrogen evolved from a specimen, as the specimen is heated in ultra-high vacuum at a constant rate from room temperature to 870 °C

Fig. 1b. Schematic of the thermal desorption spectroscopy (TDS-C) apparatus

Fig. 2. TDS-GU spectra of 3.5NiCrMoV specimens electrochemically charged at different potentials in 0.1M NaOH at 25 °C for 24 h. Specimens were discs, 8 mm in diam x 2.5 mm in thickness, prepared by water jet cutting from a round bar, and polished to 1 μm diamond.

Fig. 3. Numerical fitting performed using three Gaussian peaks for the diffusible hydrogen ($30^{\circ}\text{C} < T < 300^{\circ}\text{C}$) of the TDS-GU spectra of 3.5NiCrMoV specimens electrochemically charged at different potentials in 0.1M NaOH

Fig. 4. TDS-GU spectra of 3.5NiCrMoV specimens electrochemically charged at different potentials in 0.1M Na₂SO₄ solution at 25 °C for 24 h. Specimens were discs, 8 mm in diam x 2.5 mm in thickness, prepared by water jet cutting from a round bar, and polished to 1 μ m diamond.

Fig. 5. Numerical fitting performed using three Gaussian peaks for the diffusible hydrogen ($30^{\circ}\text{C} < T < 300^{\circ}\text{C}$) of the TDS-GU spectra of 3.5NiCrMoV specimens electrochemically charged at the stated potentials in 0.1M Na_2SO_4 solution.

Fig. 6a. TDS-C spectra for 3.5NiCrMoV steel, freshly polished to 1 μm diamond, and cathodically hydrogen charged in 0.1 M NaOH at the stated potentials for 24 h. Specimens were discs, 8 mm in diam x 2.5 mm in thickness, prepared by water jet cutting from a round bar, and polished to 1 μm diamond.

Fig. 6b. TDS-C spectra for 3.5NiCrMoV steel, freshly polished to 1 μm diamond, and cathodically hydrogen charged in 0.1 M NaOH at -2.2 V for 24 h, without and with the presence of 1.0 g L⁻¹ thiourea in the solution. Specimens were discs, 8 mm in diam x 2.5 mm in thickness, prepared by water jet cutting from a round bar, and polished to 1 μm diamond

Fig. 7. TDS-GU spectra of 3.5NiCrMoV specimens charged in gaseous hydrogen at different hydrogen pressures (2, 20, 80 and 200 bar) for 24 h. Specimens were discs, 8 mm in diam x 2.5 mm in thickness, prepared by water jet cutting from a round bar, and polished to 1 μm diamond

Fig. 8. Numerical fitting performed using two Gaussian peaks for the diffusible hydrogen ($30^{\circ}\text{C} < T < 300^{\circ}\text{C}$) TDS-GU spectra of 3.5NiCrMoV specimens charged in gaseous hydrogen at different hydrogen pressures

Fig. 9. Plot showing the fraction of hydrogen remaining in a plate of uniform thickness as a function of time, thickness, and hydrogen diffusion coefficient, D . Specimen thickness of 2.6 mm (full symbols) and 0.8 mm (open symbols) were used. The values of D ranged from $3.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ to $1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. A vertical line can be drawn at any specified time, and the intersection of the line to the curve represents the fraction of hydrogen remaining in the specimen at that time

Fig. 10. The plot of fraction of hydrogen remaining in the specimen versus time as a function of specimen thickness obtained by accounting for trap effects on hydrogen effusion. Two different values of the effective hydrogen diffusion coefficient, D_{eff} , was used: $D_{\text{eff}} = 1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at $t < 5 \text{ min}$ and $D_{\text{eff}} = 3.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at $t > 5 \text{ min}$. The vertical line drawn at 135 min corresponds to the total pre-analysis or dwell time of the specimen. The intersections of the vertical line to the two curves give an estimate of the remaining hydrogen in the steel; i.e. 0.83 and 0.46 for a specimen of thickness of $L = 2.6 \text{ mm}$ and $L = 0.8 \text{ mm}$, respectively

Fig. 11a. Plot of the total hydrogen concentration of 3.5NiCrMoV (open symbols) charged in 0.1M NaOH and 0.1M Na₂SO₄ at different overpotentials, η . The hydrogen concentrations were calculated by an integration of the area under the corresponding TDS-GU curves and corrected for hydrogen egress during pre-analysis dwell time

Fig. 11b. The total hydrogen concentration for 3.5NiCrMoV specimens electrochemically charged in 0.1M NaOH plotted against the applied overpotential, obtained from (lines are drawn to underscore trends) : (i) current study using the TDS-GU (full line), (ii) measured by Liu et al [87] (wide dash lines) and (iii) predicted using the Oriani-Dong model [87] (fine dash lines).

Fig. 11c. The plot of hydrogen concentration, obtained by numerical fitting of the peak at $T=114^{\circ}\text{C}$ and correcting for hydrogen loss, versus the overpotential for the 3.5NiCrMoV specimens electrochemically charged in (lines drawn to highlight trend): (i) 0.1M NaOH (full line) and 0.1M Na₂SO₄ (dash line). TDS-GU measurements

Fig. 12. Total hydrogen concentration for 3.5NiCrMoV specimens charged in gaseous hydrogen plotted against the square root of the charging pressure. The total hydrogen concentration was evaluated by integration of the TDS-GU peaks and corrected for hydrogen egress during pre-analysis dwell time. A two-site model for Sieverts' Law explained the positive Y-intercept as the density of already filled hydrogen traps at room temperature

Fig. 13. Total hydrogen concentration of the 3.5NiCrMoV specimens charged electrochemically with hydrogen plotted to fit the regression line for charging in gaseous hydrogen. The total hydrogen concentration is evaluated from the integration of the TDS-GU spectra and taking into account the hydrogen egress from the specimen. The manner of filling of the lower energy trap sites as shown by TDS underpins the extrapolation of the Sieverts' Law line from the gas phase charging data to the electrochemical charging data

Fig. 14a. The plot of equivalent fugacity as a function of the overpotential during charging of 3.5NiCrMoV steel in two different electrolytes. The data for this plot is derived from the total hydrogen concentration evaluated from the integration of the TDS spectra and corrected for hydrogen egress from the specimen. The right hand scale provides the hydrogen pressure related to the hydrogen fugacity.

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Fig. 14b. Plot of fugacity versus charging overpotential comparing current results (3.5NiCrMoV, TDS-GU) against the results of past studies: (i) Liu et al. (low interstitial steel) [82] and (ii) Bockris et al. [91] (Armco iron). The right hand scale provides the hydrogen pressure related to the hydrogen fugacity.

Fig. 15. The relationship between the normalised hydrogen fugacity, that is the quantity (hydrogen fugacity/hydrogen pressure), plotted against hydrogen pressure, based on the evaluation by Sezgin et al [92,93], of the equation of state (EOS) data produced by the National Institute of Standards and Technology (NIST), in particular, the isothermal density of hydrogen, $\rho(p)$, for pressures up to 20 kbar.

Fig. A1. Typical TDS-GU spectra of the hydrogen calibration standards, shown as a plot of the measured hydrogen partial pressure against temperature. TDS-GU measurements

Fig. A2. The amount of hydrogen measured by the TDS-GU plotted against the known amount of hydrogen contained in calibration standards: (i) 1 $\mu\text{g/g}$, (ii) 5 $\mu\text{g/g}$ and (iii) 2 x 1 $\mu\text{g/g}$. Adventitious water on the specimen surface can increase the measured hydrogen, as seen in the uncorrected calibration curve (dash line). The corrected calibration curve (solid line), which excludes the effect of surface-adsorbed water, is obtained by drawing a line that crosses the origin and parallel to the uncorrected line

Fig. A3. a) Hydrogen and the b) corresponding water spectra for a 5 $\mu\text{g/g}$ LECO calibration pin tested (i) as received while stored in atmosphere (squares); (ii) the same pin re-tested after desorption, without exposure to atmosphere (triangles); (iii) the same pin re-tested after 1 min of exposure (circles); (iv) the same pin re-tested after exposure to air for seven hours (diamonds). Note the increase in sensitivity by a factor 10 between hydrogen and water spectra. TDS-GU measurements.

Table 1 TDS parameter settings used during calibration and specimen analysis.

PARAMETER	CONDITION	REMARKS
Heating Ramp	2 °C/min	---
Max Temperature	870 °C	---
Dwell time in Loading chamber	120 min	A stream of UHP nitrogen is used to shroud exposed to atmosphere
Stabilization time in Analysis Chamber	15 min	To account for the pressure difference between chamber and loading chamber
Gate Valve Position	GV30	30% open
Sample Holder Status	Clean	To ensure cleanliness, sample holder was in vacuum at 870 °C

Table 2 Chemical composition (wt%) of 3.5NiCrMoV from two independent determinations, and two measurements of the mechanical properties in area [48].

Steel	Composition, wt%										Yield strength, MPa	Tensile strength, MPa
	C	Ni	Cr	Mo	V	Mn	Si	S	P	Cu		
3.5NiCrMoV	0.22	2.77	1.67	0.43	0.09	0.23	0.08	0.01	0.01	0.09	650	770
	0.21	2.75	1.65	0.41	0.09	0.22	0.07	0.01	0.01	0.09	671	793

Table 3 Total hydrogen concentrations in the electrochemically charged 3.5NiCrMoV in 0.1 M NaOH and 0.1 M Na₂SO₄ calculated by (i) integration of the whole TDS spectra and (ii) integration of 114 °C peak. The adjacent column shows the hydrogen concentration after correcting for the hydrogen lost during the pre-analysis stage. Specimens were discs, 8 mm in diam x 2.5 mm in thickness, prepared by water jet cutting from a round bar, and polished to 1 µm diamond.

Soluti on	Applied Potential , mV_{Hg/Hg2} SO4	Overpotent ial, mV	Hydrogen Concentrati on, µg/g measured from whole TDS spectra	Hydrogen Concentrati on, µg/g after H loss correction	Hydrogen Concentrati on, µg/g measured from 114°C peak	Hydrogen Concentrati on, µg/g after H loss correction
0.1 M NaOH	-1628	- 0.24	0.704	0.738	0.163	0.197
	-1728	- 0.35	0.622	0.654	0.157	0.189
	-1828	- 0.44	0.935	1.005	0.342	0.412
	-1928	- 0.54	0.961	1.034	0.356	0.429
	-2228	- 0.84	1.038	1.138	0.485	0.585
0.1 M Na ₂ SO 4	-1090	- 0.32	0.987	1.022	0.169	0.204
	-1290	- 0.52	1.173	1.259	0.422	0.508
	-1390	- 0.62	1.406	1.529	0.596	0.719
	-1490	- 0.72	1.619	1.853	1.142	1.376
	-1690	- 0.92	1.650	1.854	0.996	1.200
	-1760	- 0.99	1.682	1.932	1.222	1.472

Table 4 Total hydrogen concentrations in the gas charged 3.5NiCrMoV at different pressures calculated by (i) integration of the whole TDS spectra and (ii) integration of 114°C peak. The adjacent column shows the hydrogen concentration after correcting for the hydrogen lost during the pre-analysis stage. Specimens were discs, 8 mm in diam x 2.5 mm in thickness, prepared by water jet cutting from a round bar, and polished to 1 μ m diamond.

Charging Pressure (bar)	Sample Thickness (mm)	Hydrogen Concentration, μg/g Measured from the whole TDS spectra	Hydrogen Concentration, μg/g after H loss correction	Hydrogen Concentration, μg/g measured from 114°C peak	Hydrogen Concentration, μg/g after H loss correction
2	2.5	0.502	0.568	0.084	0.182
20	2.5	0.519	0.638	0.101	0.220
80	2.5	0.671	0.865	0.166	0.360
200	2.5	0.687	0.889	0.172	0.374

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