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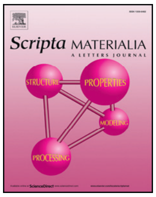

On the analysis of the simultaneous uptake and desorption of different isotopes of gaseous hydrogen by advanced high strength steels

M. Mandy [a], C. Georges [b], T. Sturel [c], P. Drillet [c], P.J. Jacques [a],*

[a] *Université catholique de Louvain, Institute of Mechanics, Materials and Civil Engineering, IMAP, 1348 Louvain-la-Neuve, Belgium*
[b] *CRM group, 4000 Liège, Belgium*
[c] *ArcelorMittal R&D, 57283 Maizières-lès-Metz, France*

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ABSTRACT

Facing the hydrogen embrittlement challenge requires the understanding of hydrogen-metal interactions. Due to its natural scarcity, the deuterium isotope is often used in dedicated experiments. When both isotopes are mutually exposed, isotopic exchanges can occur, leading to the formation of HD molecules. This work deals with the HD formation during thermal desorption analysis (TDA) of steel samples containing both hydrogen and deuterium. A method is proposed to compute the HD amount based on the H_2 and D_2 spectra measured by TDA and assessed experimentally. It appears that this HD contribution must be considered for a correct interpretation of the results.

Even though it is known for quite a long time, hydrogen embrittlement remains a major issue, particularly in the development of new grades of high strength steels for the automotive industry. Indeed, the presence of some diffusive hydrogen can strongly deteriorate the mechanical properties of sensitive microstructures [1,2]. Furthermore, the level of admissible hydrogen decreases when the global level of strength increases. Beside H_2-based reductive atmosphere imposed during annealing, other sources like water vapour, which are not necessarily controlled, can bring some diffusive hydrogen [3]. The understanding of the mechanisms of hydrogen uptake and release thus becomes of primary importance to insure viable steel grades after proper heat treatments.

When dealing with hydrogen embrittlement, the use of deuterium, the hydrogen isotope with one neutron [4], can offer several advantages. Indeed, its natural scarcity [4] guarantees that any trace of deuterium found in the considered material results from the imposed charging process. The interactions between deuterium and steels have been mostly studied in the case of stainless steels (AISI 304 and 316) used in nuclear applications, either as an alternative of the radioactive tritium [5] or coupled to hydrogen to understand the combined influence of hydrogen isotopes [6]. It has also been used more fundamentally for engineering steels [7] in the case of permeation experiments. It has thus been shown that the nature of the isotope influences several properties like diffusion [3] and solubility [7–11]. Furthermore, a specific isotopic exchange reaction is identified when both gaseous isotopes are exposed to each other and leads to the formation of hybrid molecules, such as [10,12]:

$$H_2 + D_2 \rightleftharpoons 2\ HD$$

The present study aims at assessing the analysis of uptake and diffusivity of the different isotopes of hydrogen in the case of bare 22MnB5 steel sheets. In particular, this work focuses on the right interpretation of the results provided by thermal desorption analysis (TDA) of samples containing simultaneously both isotopes. TDA is indeed a well-known method to characterize diffusive and trapped hydrogen in a material, by heating the sample to activate the diffusion and desorption of hydrogen and by quantifying its amount owing to mass spectrometers [13]. However, the simultaneous use of different sources of gaseous hydrogen has been hardly studied or mostly misinterpreted.

The mechanisms of hydrogen uptake and release could be particularly critical for the 22MnB5 steel grade used industrially in the hot stamping process carried out without any controlled atmosphere conditions [14]. Several austenitisation heat treatments were thus carried out on this steel under controlled atmospheres containing hydrogen and/or deuterium to understand these uptake and release mechanisms. TDA was then used to estimate their H and D contents. Cold-rolled 22MnB5 sheets of dimensions $200 * 200 * 1.5\ mm^3$ were heat treated at 920 °C during residence times of 10, 20 and 30 min in a muffle furnace, ensuring a controlled atmosphere, before being water quenched. The furnace atmosphere was composed of a mixture of dry nitrogen and water vapour, with or without deuterated water vapour. The

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* Corresponding author.
E-mail address: pascal.jacques@uclouvain.be (P.J. Jacques).

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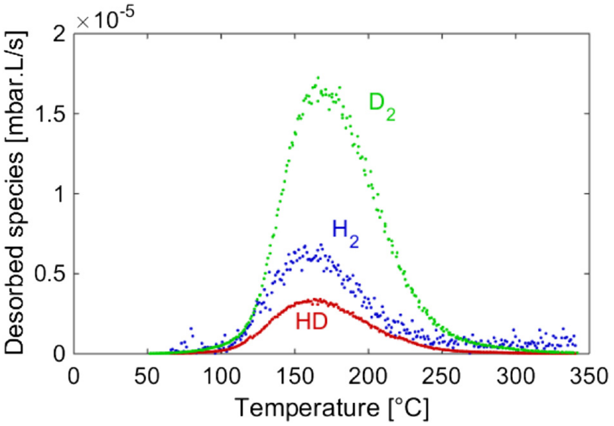

Fig. 1. Different contributions of the thermal desorption analysis of a sample containing H and D.

desired humidity was reached by bubbling dry nitrogen gas in liquid ordinary or deuterated water. Humidity was measured by a mirror hygrometer and was characterized by the dew point. Two different dew points, −10 °C and +15 °C, corresponding respectively to dry and wet atmospheres, were used for the two different gaseous mixtures: $N_2 + H_2O$ and $N_2 + D_2O$. It is worth emphasizing that in the latter case, residues of H_2O were introduced through an uncontrolled contamination of the liquid D_2O due to isotopic exchanges during exposition to atmospheric hydrogen.

After heat treatment, the steel sheets were stored in a liquid nitrogen cryotank to prevent further diffusion of atomic H and D species until the analyses. Three samples per steel sheet were finally characterized by thermal desorption analysis, by heating the sample up to 400 °C at a heating rate of 20 °C/min. During heating, a dry nitrogen gas sweeps the sample, so that desorbing H and D atoms recombine and are brought to a mass spectrometer. This device quantifies the gaseous H_2 and D_2 contents of the nitrogen flux, owing to calibrations carried out twice a day by certified standard gases of N_2-50 ppm H_2 and N_2-50 ppm D_2. By integrating the resulting spectra up to 350 °C (i.e. the end of the diffusive peak), the amounts of hydrogen and deuterium are computed and expressed in terms of mass ppm. Since deuterium is twice heavier than hydrogen, it is preferred to compare them as molar or atomic ppm. In this work, the resulting diffusive amounts are thus expressed as moles of H or D per 10^6 g of steel.

During the TDA, atomic species H and D thus desorb and recombine as H_2, D_2, but also as hybrid HD molecules, as shown on Fig. 1, where the H_2, D_2 and HD desorption spectra are given as a function of the temperature. The contents of H_2 and D_2 molecules can then be calculated owing to the calibrated mass spectrometers. Nevertheless, even though HD can also be detected by the mass spectrometer, no certified gas is in contrast available to quantify the HD amount. For this reason, the amount of desorbed species shown on the spectra of Fig. 1 is expressed in the units of the mass spectrometer, that is mbar·L/s.

Even though the HD content cannot be quantified experimentally, it can nevertheless be deduced from the experimental H_2 and D_2 desorption spectra obtained by TDA. The proposed method is inspired from the work of San Marchi et al. [12]. It assumes that the thermodynamic equilibrium is reached in the gas phase resulting from the desorption of both species from the steel sheet. Based on this hypothesis, the equilibrium constant K_{eq} of the reaction $H_2 + D_2 \rightleftharpoons 2\,HD$ allows writing:

$$K_{eq} = \frac{p_{HD}^2}{p_{H_2}\ p_{D_2}} \Longleftrightarrow y_{HD} = \sqrt{K_{eq}\ y_{H_2}\ y_{D_2}}$$

where p_i and y_i correspond to the partial pressure (in atm) and to the molar fraction of the compound i, respectively. This equation assumes that the activities of the different compounds are equal to their molar fractions, which holds for an ideal solution. The value of K_{eq} was found in the HSC database [15] and is expressed as:

$$K_{eq} = \ exp\left(\frac{-(-11.91\,T + 728.83)}{RT}\right)$$

where T is the temperature in Kelvin and R the ideal gas constant, 8.314 J/(mol K). Owing to these equations, it is thus possible to recalculate the theoretical spectrum of HD by computing the HD content in equilibrium with the H_2 and D_2 amounts desorbed at each temperature and measured by the TDA spectrometers. The total HD amount is then found by integrating this HD spectrum.

Even though this method allows computing easily the HD amount based on the experimental knowledge of H_2 and D_2 contents, it relies on strong hypotheses. It firstly supposes that the equilibrium between H_2, D_2 and HD is reached in the time period between the desorption of the atomic H and D species from the material and their arrival at the mass spectrometer probe. It also implies that the gas flux in which H and D are carried out does not prevent from achieving the equilibrium. Furthermore, it is assumed that the sole compounds allowed to be formed in the TDA are H_2, D_2 and HD, i.e. no potential contamination with oxygen is considered. Finally, it is worth emphasizing that this computation method does not depend on the material and can thus theoretically be extended to any metal.

Fig. 2 presents the total diffusive contents (in terms of the sum of H and D moles per 10^6 g of steel) as a function of the residence time in the furnace (which includes the heating and the holding stages) and of the atmosphere composition. As mentioned above, 4 compositions of atmosphere have been studied. The solid lines represent chargings with $N_2 + H_2O$, while the dashed lines correspond to the $N_2 + D_2O$ (+H_2O) atmosphere. In both cases, the lightest curves refer to a dew point of −10 °C, whereas the darkest curves correspond to the dew point of +15 °C

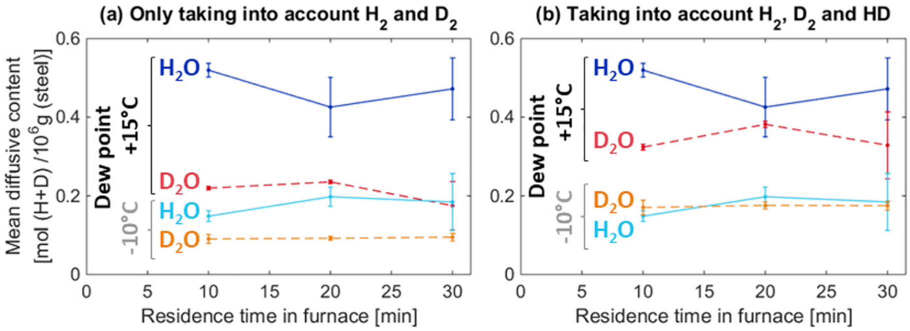

Fig. 2. Mean diffusive contents (expressed as the sum of desorbed H and D) as a function of the residence time and of the atmosphere composition by (a) only taking into account the H_2 and D_2 contributions and (b) by adding the HD contribution to previous results.

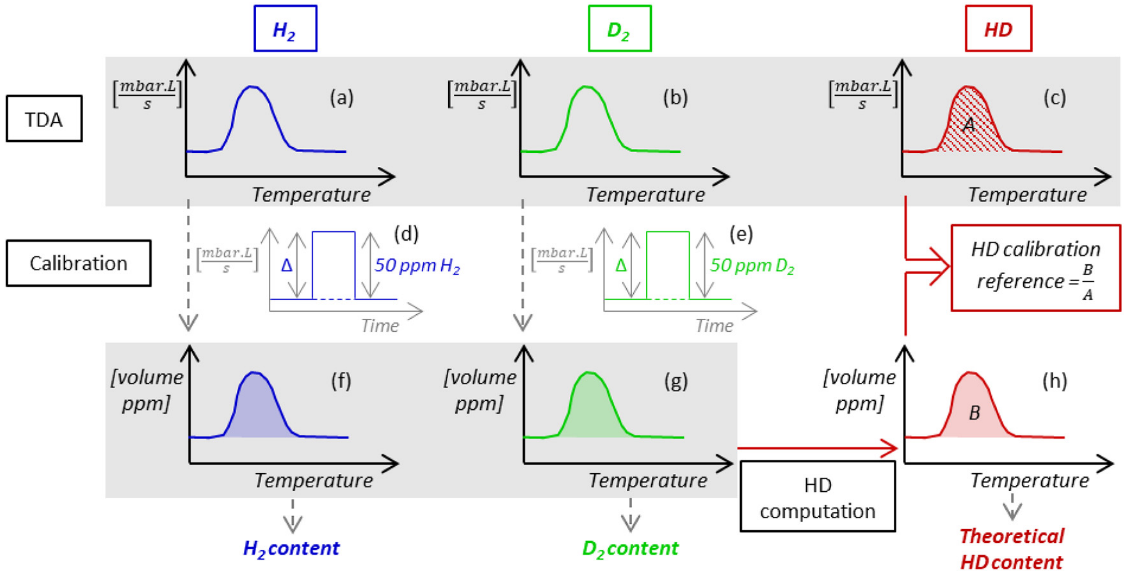

Fig. 3. Schematic representation of the methodology developed to compare experimental results and theoretical computations.

for each type of atmosphere. Each point corresponds to the mean value of three analysed samples and the error bar gives the standard deviation with respect to the mean value. On Fig. 2(a), the desorption and recombination into only H_2 and D_2 molecules are considered, while on Fig. 2(b), HD molecules are also taken into account when relevant. In this latter case, the HD contribution is computed owing to the method proposed above and is added to the total diffusive content. It is straightforward to see that the curves related to $N_2 + H_2O$ uptakes are the same on both graphs as samples only contain hydrogen.

Fig. 2 allows highlighting the strong influence of the existence of HD molecules on the interpretation of the results. Indeed, Fig. 2(a) shows, for the different residence times, a diffusive content approximatively twice more important in the case of a H_2O uptake than in the case of a D_2O uptake for the same dew point. This would mean that the isotope effect on solubility is so strong that the amount of atoms of hydrogen entering in the steel sheet is about twice the amount of deuterium atoms at a given dew point. However, contrarily to these considerations, when HD is taken into account (which is observed on Fig. 2(b)), the difference of diffusive contents related to D_2O and H_2O uptakes is drastically reduced, so that they are now of the same order of magnitude. These results clearly prove the importance of taking into account the recombination into HD molecules during TDA.

When comparing both atmospheric sources of hydrogen (i.e. H_2O or D_2O) at iso-dew point, it is worth noting that an isotope effect is observed on the temperature – partial pressure relationship [16,17], which relates the dew point and the corresponding water vapour pressure in the atmosphere. This thus implies that a given dew point actually corresponds to a higher partial pressure of H_2O than of D_2O in the atmosphere. In particular, a dew point of $+15$ °C corresponds to 1.68 vol% of H_2O or to 1.42 vol% of D_2O, while the dew point of -10 °C corresponds to 0.26 vol% H_2O or to 0.19 vol% D_2O. Considering the Dalton's law to transform the partial pressure into molar percentages, these conversions are obtained owing to different relationships developed in the literature for ordinary [16,18] or deuterated [16,19] water vapours in equilibrium with their solid or liquid phases. Due to this isotope effect, it cannot be directly concluded from Fig. 2 that a same content of ordinary or deuterated water vapour in the atmosphere leads to the same diffusive contents.

In order to assess the reliability of the HD computing method, theoretical HD computation was compared with measured HD spectra following the methodology described in Fig. 3. This comparison aims at providing a calibration reference for the quantification of HD from mass spectrometer results. Indeed, in the case of H_2 and D_2, a calibration reference is used to quantify the data registered by the spectrometer, i.e. to transform the experimental TDA spectra (Fig. 3(a) and (b)) into quantitative data (Fig. 3(f) and (g), respectively). A three-point calibration of the device is made, according to the principle highlighted on Fig. 3(d) and (e): for each compound (H_2 or D_2), the background of the mass spectrometer is measured while injecting dry nitrogen gas. A certified standard gas of $N_2 + 50$ ppm of X_2 (X standing for the isotopes H or D) is then injected during a given time (about 3 min) and the background is finally measured again after stopping the standard gas injection. The mean background value is defined as a line delimitated by the background values measured before and after the certified gas injection. The difference Δ between this mean background value and the mean spectrometer value measured during injection is calibrated to correspond to 50 ppm, the known content of the certified gas (Fig. 3(d) and (e)). Calibration references, ref_{X2}, with X being equal to H or D, can then be defined as:

$$ref_{X_2} = \frac{50}{\Delta_{X_2}} \left[\frac{ppm}{mbar.L/s}\right]$$

Table 1 gives the mean values of the calibration references for H_2 and D_2, resulting from several repetitions of the calibration procedure of the mass spectrometers.

Based on the same idea, a calibration reference for HD can be defined for a given sample by comparing the computed HD spectrum with the experimentally measured spectrum. The comparison criterion between the theoretical and measured spectra considered here consists in the integral of the desorption peak up to 350 °C. The calibration reference for HD is thus established as the ratio between the peak integrals of the computed (Fig. 3(h)) and experimental (Fig. 3(c)) spectra. The reliability of the method can be assessed owing to the comparison of the

Table 1
Summary of the calibration references measured experimentally for H_2 and D_2 and computed for HD.

	Mean calibration reference $[\frac{ppm}{mbar.L/s}]$	Standard deviation [%]	Number of measurements [−]
H_2	$8.3\ 10^6$	9	139
D_2	$5.4\ 10^5$	5.3	37
HD	$4.6\ 10^6$	7.9	26

calibration references computed from a large number of samples. The mean value of the calibration references carried on samples of bare 22MnB5 steel is given in Table 1, as well as the standard deviation and the number of samples. The standard deviation of the HD calibration reference is comparable to the ones determined experimentally for H_2 (9%) and D_2 (5.3%). It thus brings some confidence in the calibration procedure. Furthermore, the calibration reference computed for HD also approximatively corresponds to the average of experimentally determined calibration references of H_2 and D_2 ($4.4\ 10^6$ ppm/(mbar·L/s)), which is the hypothesis considered by Wang et al. [20] for their calibration of HD measurement.

Even if no influence on the results has been observed, it is worth noting that the HD calibration references are actually not independent but paired two by two. Indeed, only two mass signals are detected on the used TDA set-up, each one being able to record the data for one compound (H_2, D_2 or HD). Henceforth, two analyses are necessary to establish the full desorption spectra of the three compounds. However, as TDA is a destructive method, those two analyses had to be carried out on two different samples, which were adjacent on the raw heat treated steel sheet. The hypothesis that both samples present the same diffusive content is thus considered. For both samples, the HD experimental spectrum has been measured, while the H_2 spectrum has only been measured on one sample and the D_2 spectrum on the other. Both H_2 and D_2 spectra allowed computing a theoretical HD spectrum, which is compared to both experimental spectra measured on the two samples, leading by this way to two different calibration references.

Owing to this validated computation of the HD contribution, a first step towards the analysis of hydrogen embrittlement helped by the use of deuterium is overcome. This work indeed shows how to take into account the specificities of deuterium combined with the presence of hydrogen.

Acknowledgments

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