

Ultrasonic Metrology for the Study of Hydrogen Embrittlement in Steels

Louis Leffray¹, Guy Feuillard¹, Jules Toupin¹, Hossep Achdjian¹, Julien Bustillo¹, and Nicolas Mary²

¹GREMAN Laboratory, INSA Centre Val de Loire, UMR CNRS 7347. Université de Tours. 3 rue de la Chocolaterie 41034 Blois Cedex France

²MATEIS, INSA Lyon, UMR CNRS 5510 Bât. B. Pascal, 4^o étage 7, Avenue Jean Capelle 69621 Villeurbanne Cedex France
guy.feuilleard@insa-cvl.fr

Abstract: In this work, we propose the development of an ultrasonic metrology system that allows for real-time measurements of velocity in steels during electrochemical hydrogen charging. This study is coupled with a propagation model in a water-steel-water structure. For 2% variation of the stiffness coefficient when the material is fully charged in hydrogen, we simulate a variation of a few dozen meters per second due to property changes. We report the measurement of velocity variations conducted on a DP800 dual-phase steel. When the effect of the temperature on the velocity measurement is compensated, the standard deviation for the velocity measurement is less than $0.2 \text{ m}\cdot\text{s}^{-1}$. Experiments were conducted in DP800 dual-phase steel over several tens of hours of electrochemical charging of steel immersed in a hydrogenocarbonate solution on two samples. A hardening of the material is observed, with velocity an increase of $25 \text{ m}\cdot\text{s}^{-1}$ in one sample and $45 \text{ m}\cdot\text{s}^{-1}$ in the second one.

Keywords: Ultrasonic metrology system, Hydrogen Embrittlement, velocity measurement.

Introduction

Hydrogen-steel interactions are widely documented in the literature, and regardless of the proposed mechanism, the conclusions remain identical, with the creation of microstructural defects (dislocations, microstructural changes, atomic decohesion) [1]. As a result, the mechanical properties of materials are degraded. The elastic limit of a material is then lowered, leading to premature failure of the structure. Techniques for assessing a steel's sensitivity to hydrogen trapping and diffusion are well known and are largely based on electrochemical charging tests. Although there are only a small number of mechanical tests coupled with electrochemical charging [2], these provide access to the reaction mechanisms involved in hydrogen embrittlement but are not suitable for on-site health monitoring. To achieve this, we need to consider the use of non-destructive testing techniques capable of detecting and quantifying any metallurgical modifications related to the absorption of hydrogen in a metal structure. Among the available methods for characterizing mechanical properties, ultrasonic methods are widely known and used. They can be used in transmission or reflection modes and are based on the analysis of the time arrival and amplitude of the received signal.

In this work, we propose the development of an ultrasonic metrology system that enables real-time mea-

surements of velocity variations in steel samples during hydrogen charging. In the first section, an electroacoustic model is proposed to predict the transmitted pulse response on the receiving transducer. The material and experimental setup are presented, with particular attention given to the description of the ultrasonic setup coupled with electrochemical charging. Finally, we report initial results on velocity variations in two dual-phase steels (DP800).

Modelling

Assuming a plane ultrasonic wave, the propagation in a multilayer structure can be described by a transfer matrix formalism. Considering a structure consisting of n layers, each layer, i , is described by a transfer matrix given by Eq. (1)

$$[M_i] = \begin{bmatrix} \cos(k_i L_i) & -j Z_i \sin(k_i L_i) \\ -\frac{j}{Z_i} \sin(k_i L_i) & \cos(k_i L_i) \end{bmatrix} \quad (1)$$

Where Z_i is the acoustic impedance of the medium given by the product of the density by the ultrasonic phase velocity, k_i is the wave number, L_i is the thickness of the layer, and j is the complex number. The total transfer matrix system is given by the product of the matrices Eq. (2)

$$[M_{\text{tot}}] = \prod_{i=1}^n [M_i] \quad (2)$$

This multilayer structure is excited by a pressure source P_1 , giving rise to particle velocity v_1 from a transducer of internal acoustic impedance Z_t . The multilayer is closed on the acoustic impedance of the receiving transducer Z_s (Fig. 1). P_e is the excitation pressure, P_2 , v_2 the pressure and the particle velocity at reception.

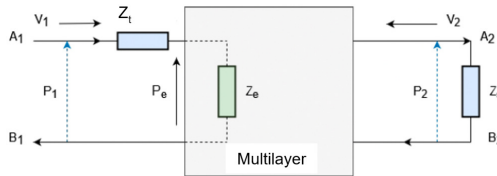


Fig. 1: Equivalent scheme for transfer function calculation.

Denoting A , B , C , D the components of $[M_{\text{tot}}]$ we have Eq. (3).

$$\begin{pmatrix} P_e \\ V_1 \end{pmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{pmatrix} P_2 \\ -V_2 \end{pmatrix} \quad (3)$$

Knowing that $V_2 = P_2/Z_s$, the transmission transfer function is given by Eq. (4)

$$H_t(f) = \frac{P_2}{P_e} = \frac{1}{A - \frac{B}{Z_s}} \quad (4)$$

For a given excitation signal, $x(t)$, the frequency transmitted pulse response is obtained by multiplying the transfer function $H_t(f)$ by the spectrum of the excitation signal. The time response then is obtained by taking the inverse Fourier transform. For all the simulations, we have chosen a Gaussian excitation signal centered on the transducer's center frequency.

Experimental set-up

In our study, a commercial DP800 dual – phase steel was used. DP800 is mainly made of ferrite and martensite steel with a lower content of bainite. Typical value reported in literature [3] for the volume fraction of each component is 69% of ferrite 30% of martensite and less than 1% of bainite. Samples used for the experiment were 1 mm thick with lateral dimensions of $50 \times 30 \text{ mm}^2$.

The experimental set-up is shown in Fig. 2. Hydrogen charging was performed by an electrochemical technique using a three-electrode configuration. Steel samples (i.e., the working electrode) were connected to a potentiostat (*Biologic, MPG2, Seyssinet-Pariset,*

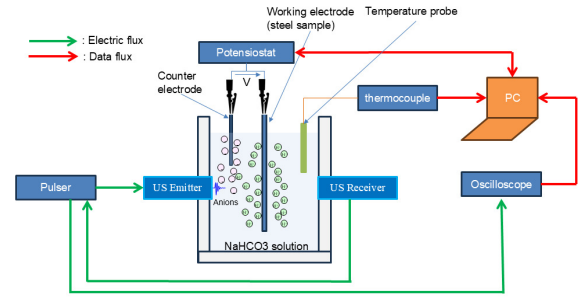


Fig. 2: Experimental setup diagram.

France). The counter electrode was a Platinum plate, and the reference electrode was an $Ag/AgCl$ secondary reference electrode ($E = +237 \text{ mV}/ESH$). The charging electrolyte was a solution of $NaHCO_3$ with a concentration of 0.5 M at room temperature. To control the physico-chemical state of the surface before charging, a surface conditioning step was used. During experiments, a potential scan until -1.2 V vs $Ag/AgCl$ at a scan rate of $100 \text{ mV}/s$ is applied. Finally, the charging potential was maintained at -1.2 V vs $Ag/AgCl$ for several tens of hours.

The ultrasonic measurements were carried out in normal incidence. The setup consists of two 50 MHz ultrasonic transducers (*Olympus Panametrics - NDT V358 50MHz/0.25*), one used as an emitter and the second one as a receiver. Electrical excitation was provided by a Panametrics Model 5601A/TT pulser receiver. The received signals were acquired by a digital oscilloscope (*Rohde & Schwarz RTB2004, Munich, Germany*) at a sampling frequency of 2.5 GHz , with an averaging over 1024 acquisitions and then transferred to a computer for processing on Matlab. Simultaneously with hydrogen charging and ultrasonic measurements, the temperature was measured using a $Pt100$ temperature probe connected to its conditioner and transferred to the computer. A typical transmitted signal is presented in the red curve Fig. 3. The first echo corresponds to the ballistic pulse, i.e., the direct transmission, and the following successive echoes correspond to the round-trip into the steel sample. During hydrogen charging, both changes in velocity and attenuation are expected. However, due to the presence of hydrogen bubbles in the medium, only velocity measurements were carried out. The ultrasonic longitudinal wave velocity in steel (Eq. (5)), v , is related to the Time Of Flight (TOF) between two echoes Δt and the thickness, e , of the sample.

$$v = 2 \frac{e}{\Delta t} \quad (5)$$

During experiments, a good signal-to-noise ratio is observed, and the TOF is then determined by tak-

ing the average TOF between two successive echoes determined by cross-correlation until the tenth echo. With a sampling frequency of 2.5 GHz , a sample thickness of 0.95 mm , and an ultrasonic longitudinal wave velocity of $6000\text{ m}\cdot\text{s}^{-1}$ in the material (which is typical for steel materials), the induced error on the velocity measurement due to a mislocation of the maximum of cross-correlation is approximately $\pm 7\text{ m}\cdot\text{s}^{-1}$ per time sample. This error is too large for accurate monitoring of the ultrasonic velocity in the sample, where variations of about $20\text{ m}\cdot\text{s}^{-1}$ are expected. To improve time-of-flight estimation accuracy, the signal is oversampled by a factor of 100 using the *Makima* interpolation method in MATLAB.

Results and discussions

Fig. 3 shows the comparison between experiments and simulations for an uncharged DP800 sample. For the simulations, the properties are given in Tab. 1 for steel.

Tab. 1: Simulation parameters.

Gaussian Signal		
A_0	σ	f_c
1	2.10^{-8}	50 MHz
Material properties		
	Velocity	Acoustic impedance
Water	$1500\text{ m}\cdot\text{s}^{-1}$	1.5 MRayl
DP 800	$6062\text{ m}\cdot\text{s}^{-1}$	47.59 MRayl

The positions of the echoes within the sample are accurately predicted; however, the amplitudes differ, as the attenuation of the ultrasonic waves in the steel was not precisely taken into account in the model. Additionally, the shape of the simulated echoes differs from that of the experimental ones. This discrepancy is attributed to the use of a Gaussian waveform in the simulations. Hydrogen charging results in a hardening of the material. For DP800 steel, the literature reports an increase in the stiffness coefficient of a few percent, corresponding to a similar change in ultrasonic velocity [4]. In this study, we considered a 2% increase in the stiffness coefficient for a fully hydrogen-charged steel. This variation leads to a velocity increase of approximately $16\text{ m}\cdot\text{s}^{-1}$, which is well within the resolution achievable with the algorithm used for velocity measurements.

Electrochemical hydrogen charging of steels is a diffusion-driven process with kinetics that can span several days. It is therefore essential to control the temperature and assess its impact on the measurements. To this end, we conducted an initial experiment in which we measured the ultrasonic wave velocity in the steel as a function of time and temperature,

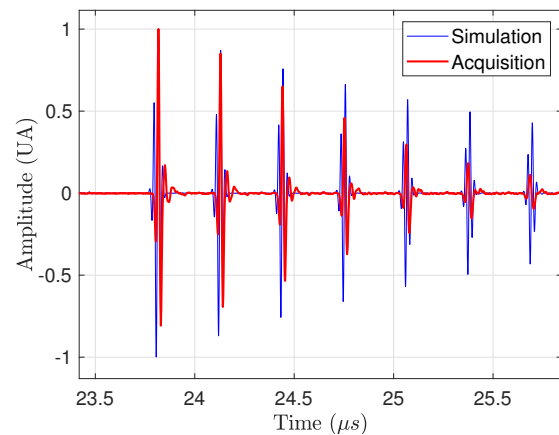


Fig. 3: Experimental and simulated transmitted signal through uncharged DP800 steel.

without hydrogen charging. Fig. 4 shows the evolution of velocity as a function of temperature in steel over a 48-hour measurement period. During this period, the temperature varied between 21 and 25°C , and we observed a linear dependence of the velocity on this temperature. The temperature coefficient is $0.68\text{ m}\cdot(\text{s}\cdot^\circ\text{C})^{-1}$, consistent with what is reported in the literature for steels [4]. When the temperature is compensated over the given period (Fig. 4), the variance on the measurement of the velocity is $0.13\text{ m}\cdot\text{s}^{-1}$, which should allow for monitoring the hydrogen charging.

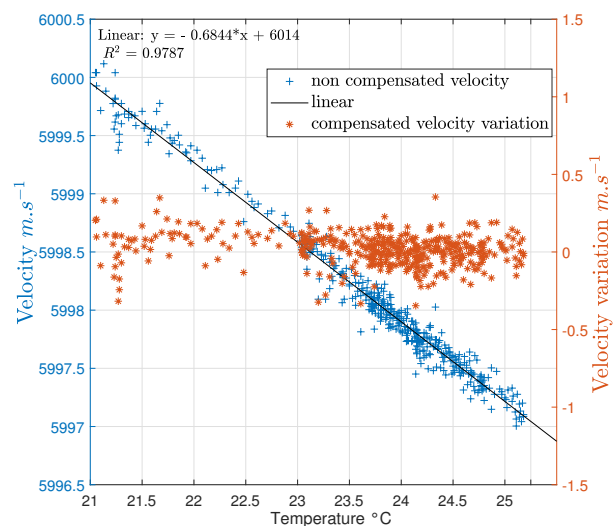


Fig. 4: Ultrasonic wave velocity in the DP 800 steel sample as a function of temperature and temperature-compensated velocity variations.

Fig. 5-a and Fig. 5-b show the temperature-compensated variations in velocity observed during

hydrogen charging on two DP800 samples. We also show the evolution of the current in the solution. For these measurements, the reference velocity was determined after 60 *mn*, after the temperature and the short-time current began to stabilize in the measurement cell. Hydrogen charging times are 120 hours for the first measure and 55 hours for the second. During the experiments, it was necessary to periodically refill the measurement cell with water due to significant water evaporation over time, which led to current fluctuations during the second measurement. However, it is important to note that the electrochemical potential remained below the threshold required for hydrogen charging. Current fluctuations are attributed to the formation of gas bubbles on the surface of the counter-electrode and to the evaporation of water, which alters the immersed surface area of the counter-electrode. These phenomena explain the noise observed in the current curves. For the first measurement, we observed an increase in velocity variation of $25 \text{ m}\cdot\text{s}^{-1}$ with a plateau appearing after 50 hours of experiment. This plateau corresponds to a stabilization of the current at -10 mA that seems to indicate that the charging in this sample is complete. It should be noted that this sample had previously been used for electrochemical hydrogen charging tests, and we cannot guarantee that it is completely blank. As reported in the literature, we observed an increase in the ultrasonic velocity and a stiffening of the steel. For the second measurement, we worked on a blank sample and observed a $40 \text{ m}\cdot\text{s}^{-1}$ velocity variation. However, we did not observe a plateau at the end of the 50-hour experiment. For this sample, the relative velocity variation is around 0.7%, corresponding to a relative increase of the stiffness coefficient of 1.4%.

Conclusion

In this study, we have demonstrated that ultrasonic measurements represent a promising non-destructive technique for monitoring hydrogen uptake in steel by observing variations in ultrasonic velocity during hydrogen diffusion. We report maximum velocity variations of $25 \text{ m}\cdot\text{s}^{-1}$ and $45 \text{ m}\cdot\text{s}^{-1}$. Given the precision achieved through temperature compensation, these changes can be attributed to hydrogen migration within the steel samples rather than to temperature fluctuations. To date, the experiments have been limited to a single steel grade. Literature suggests that the response to hydrogen charging may vary depending on the steel composition. Further investigations are warranted to generalize these findings.

References

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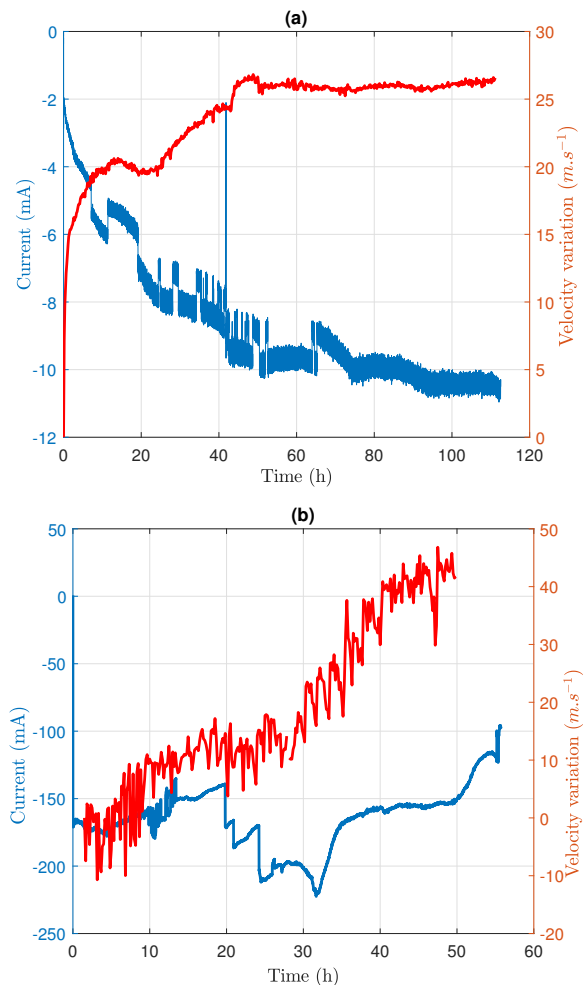


Fig. 5: Velocity variation in DP 800 steel and current into the electrochemical bath for the two samples.

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