HELIOS: A NEW METHOD FOR HYDROGEN PERMEATION TEST

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ABSTRACT
Hydrogen induced cracking is still a severe and current threat for several industrial applications. With the aim of providing a simple and versatile device for hydrogen detection, a new instrument was designed based on solid state sensor technology. New detection technique allows to execute hydrogen permeation measurement in short time and without material surface preparation. Thanks to this innovation, HELIOS offers a concrete alternative to traditional experimental methods for laboratory permeability tests. In addition, it is proposed as a new system for Non Destructive Testing of components in service in hydrogenating environment. Hydrogen flux monitoring is particularly relevant for risk mitigation of elements involved in hydrogen storage and transportation. Hydrogen permeation tests were performed by means of HELIOS instruments both on a plane membrane and on the wall of a gas cylinder. Results confirmed the extreme sensitivity of the detection system and its suitability to perform measurements even on non metallic materials by means of an easy-to-handle instrument.

1.0 INTRODUCTION

HELIOS instruments (Letomec srl, patent pending) are designed for safety monitoring of plants, components and systems for energetic purpose. Such a demand is particularly pressing due to the expected diffusion of Hydrogen Economy and the general drive of automotive industry towards hydrogen vehicles commercialization on a large scale. HELIOS idea arose from several industrial partnerships and academic projects that highlighted the demand for specific solution for hydrogen detection in engineering materials from the beginning to the end of manufacturing, involving laboratory analysis and process control systems. As a matter of fact, HELIOS is the result of twenty-five years of experimental activity in the field of hydrogen degradation of steels. During this period, the subject was investigated by means of several techniques both in laboratory and industrial conditions. Unfortunately, the majority of the available apparatus and methods present intrinsic limits related to the technology used for hydrogen detection [1] and permeability analysis. Nowadays, the availability of a new generation of solid state metal oxide sensors [2] makes possible to design versatile solutions for a wide range of applications and to simplify instruments architecture and test procedures. Metal oxide sensing mechanism is based on H_2 gas-solid interactions that result in a change in electron (or hole) density at the surface, which in turn results in a change in overall conductivity of the semiconductor oxide. Essentially, HELIOS main innovation is to realize a system for hydrogen detection free from practical drawbacks of traditional electrochemical devices (that is working with liquid solutions, electrodes, fragile parts, and the like) [3,4], applicable only to some metals. One of HELIOS advantages is the independence of detection performance from surface quality. This is especially relevant for permeability test to be performed on steel parts currently performed by the well known Devanathan-Stachurski [5] set-up. Thanks to this, Non Destructive Testing can be carried out in critical environments by an inexpensive and time saving method. In the present work, two versions of HELIOS were used: HELIOS II and IV which are a permeation cell and a diffusible hydrogen flow-meter respectively. Analysis performed by means of HELIOS II provided the parameters necessary to characterize the interaction between hydrogen and X52 steel, which is a low strength material largely used for hydrogen cylinders and pipes. Subsequently, HELIOS IV was used to measure, for the first time, the hydrogen emanated from the wall of a hydrogen cylinder in service. Additional gaseous hydrogenation and thermal desorption analysis were carried out with the aim of verifying HELIOS IV results.

2.0 EXPERIMENTAL

The object of the study is X52 grade steel whose chemical composition is listed in Table 1.

Table 1. Chemical composition of X52 steel.

Element	C	Mn	Si	Cr	Ni	Mo	S	Cu	Ti	Nb	Al
Wt. %	0.206	1.257	0.293	0.014	0.017	0.006	0.009	0.011	0.001	0.03	0.034

A permeation membrane was tested by means of HELIOS II permeation apparatus visible in Figure 1.

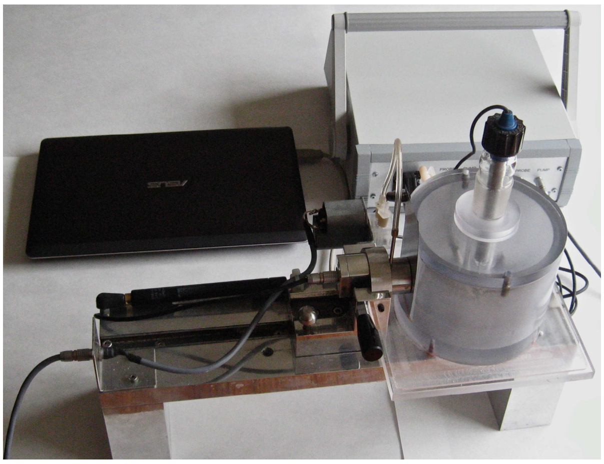

Figure 1. HELIOS II layout.

The instrument is composed by a semi-cell for hydrogen generation, a steel probe, containing the solid state sensor which is connected to an electronic controller and a dedicated PC for data logging and processing. Electrochemical permeation analysis was carried out on a membrane mounted as a working electrode, between the semi-cell and the probe which replaces the traditional detection semi-cell. Hydrogen charging conditions were: H_2SO_4 0.1N and As_2O_3 10 g/l (added as a hydrogen recombination poison) with a cathodic current density of 10 mA/cm^2. In addition, a permeability test was carried out, by means of HELIOS IV apparatus, on a gas cylinder containing H_2 at 60 bar. As shown in Figure 2 (a), the instrument consists in an aluminium probe equipped of a magnetic connection and a silicon O-ring on the entry side. Measurement configuration is visible in Figure 2 (b). Test were performed at room temperature and without preliminarily preparation of the painted surface. Before testing, a stainless steel thin sheet was inserted between the probe and the cylinder surface in order to prevent hydrogen detection and set a background value of the signal. The barrier was inserted even during the permeation test with the aim of observing the resulting effect on hydrogen flux signal. For the last series of test, some plane specimens underwent to gaseous hydrogenation in autoclave, as shown in Figure 3. Charging was performed at three different pressures (50, 100 and 150 bar) for one week each, in order to achieve hydrogen saturation condition for the steel. After the autoclave treatment, specimens were analysed by means of LECO DH603 thermal desorber to measure hydrogen concentration.

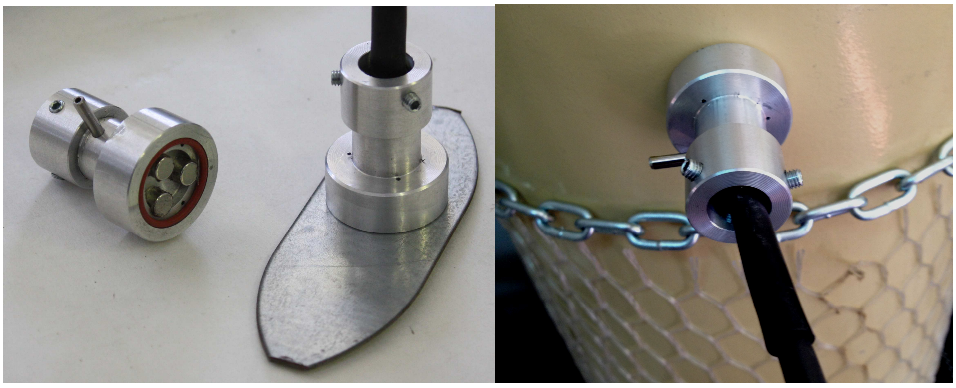

Figure 2. (a) HELIOS IV probe; (b) and experimental set-up for cylinder measurement.

Figure 3. Autoclave and specimens used for gaseous hydrogenation.

3.0 RESULTS AND DISCUSSION

The current-time curve registered by HELIOS II during the electrochemical permeation is shown in Figure 4. Time-lag method [6] was used to calculate the hydrogen diffusion coefficient, from the permeation curve, applying the relation (1):

$$D = \frac{L^2}{(6 \cdot t_L)}, \qquad (1)$$

where D – diffusion coefficient, cm^2/s; L – thickness, cm; t_L – time lag, s.

From the calculation, the diffusion coefficient for X52 steel resulted 2.5±0.5E-6 cm^2/s. Results from HELIOS IV tests are plotted in Figure 5. The evident alternating trend of the signal represents the sequence of measurements performed with or without the stainless steel barrier between one hydrogen measure and another. It was detected a hydrogen flux in ranging between 150 and 135 $pl/cm^2/s$ where volume is expressed in picoliters according to the equivalence 1 pl = 4.46E-14 mol of hydrogen at standard conditions for temperature and pressure. From experimental data, C_H (expressed in wppm that is Weight Parts per Million) can be calculated by Fick's law at the steady state (2):

$$J = D\frac{C_H - C_{EX}}{L}, \qquad (2a)$$

$$C_H = \frac{J \cdot L}{D}, \qquad (2b)$$

where J – hydrogen flux, wppm/cm^2/s; C_H – concentration at the entry side, wppm; C_{EX} – concentration at the exit side, wppm; D – diffusion coefficient, cm^2/s; L – thickness.

The diffusion coefficient in (2) is the same calculated by (1) and so it is relative to a planar geometry although the cylindrical symmetry of the problem. Nevertheless, due to the small area interested by the probe, assuming a similar approximation is reasonable. Taking into account that hydrogen concentration in air, that is C_{EX}, is negligible, C_H absorbed by cylinder wall amounts to 0.24-0.22 wppm for the maximum and the minimum value of flux respectively. As far as gaseous charged specimens are concerned, their hydrogen concentration was measured and plotted as a function of hydrogenation pressure. Data were extrapolated according to Sievert's law (3) assuming zero hydrogen concentration at zero partial pressure, that is bounding the fit to the origin. Resulting fit, shown in Figure 6, provides the value of the constant A which expresses the relationship between hydrogen concentration and hydrogen partial pressure.

$$C_H = A \cdot \sqrt{P_{H_2}}\ , \qquad (3)$$

where C_H – hydrogen concentration, wppm; A – material constant at room temperature, wppm/bar$^{1/2}$; P_{H2} hydrogen partial pressure, bar.

Then, substituting P_{H2} = 60 bar and A = 0.029 wppm/bar$^{1/2}$ in (3), it results C_H = 0.22 wppm, in very good agreement with the hydrogen concentration on the internal surface of the cylinder previously calculated.

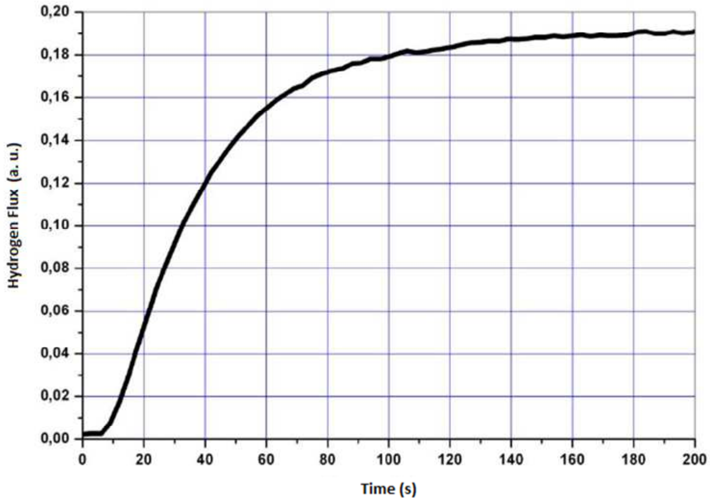

Figure 4. Hydrogen permeation curve for X52 steel.

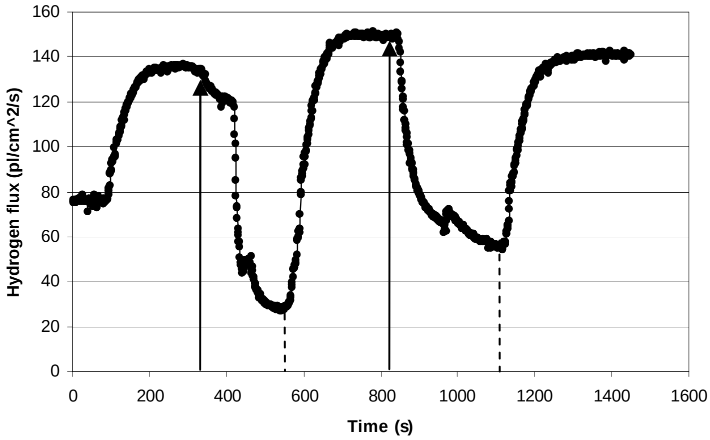

Figure 5. Hydrogen signal related to cylinder test. Arrows mark where the stainless steel barrier was temporarily inserted to stop hydrogen flux to be detected by HELIOS whereas dotted lines mark barrier removal.

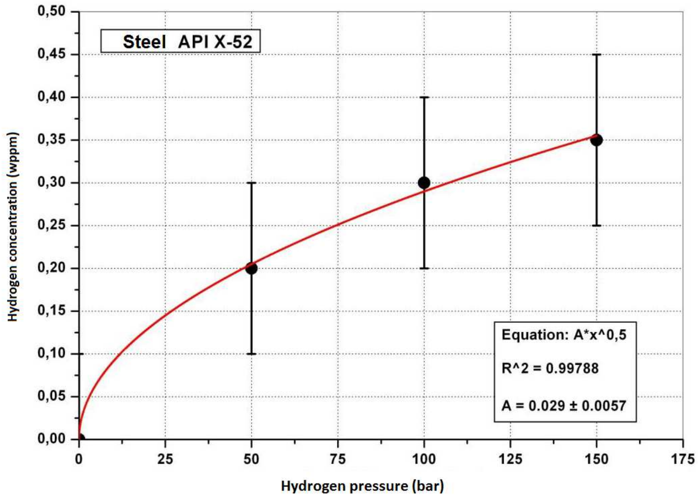

Figure 6. Hydrogen concentration (wppm) vs hydrogen pressure (bar).

3.0 CONCLUSIONS

1) Diffusion coefficient, equal to 2.5±0.5E-6 cm^2/s, was measured for X52 steel by means of a solid state sensor detection system.

2) Hydrogen flux through a gas cylinder wall was detected with no preliminary surface preparation.

3) Hydrogen concentration values, obtained by mathematical elaboration of HELIOS IV data, are coherent with the results of the analysis carried out according to Sievert's theory.

4) Measurement on the painted wall of the cylinder demonstrated that HELIOS instruments are provided of an extreme sensitivity. Due to this, they can be usefully employed to measure very low hydrogen flux in operative conditions related to hydrogen storage and transportation.

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