Effect of hydrogen content in natural gas blend on the mechanical properties of a L485-MB low-alloyed steel

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ABSTRACT

The purpose of the present work is to study the effect of the hydrogen content in a H_2-NG (Natural Gas) blend on the mechanical behavior of a C-Mn low alloy steel L485-MB (NF EN ISO 3183) under monotonic loading. Different testing conditions were explored for the blend: 2%H_2-NG, 25%H_2-NG, 100%H_2 and 100%NG at a total pressure of 8.5 MPa using two slow strain rates: 10^{-4} s^{-1} and 10^{-6} s^{-1}. Tests in the blend were compared to those under pure hydrogen at the same partial pressures. Furthermore, two surface roughnesses have been explored, one corresponding to a mirror polish, the other as lathed. The embrittlement has been assessed by necking measurements and fracture analysis for the whole testing conditions. The results show a drop of ductility with the increase of partial pressure of hydrogen in natural gas. Besides, no significant effect of hydrogen were observed on flow stress. In addition, the L485-MB pipeline steel presents a shear type fracture mode in high partial pressure of hydrogen, whereas a cup and cone type fracture were observed in air, natural gas and low partial pressure of hydrogen in natural gas (0.2MPa H_2).
Keywords: Hydrogen embrittlement, low alloy steel, H_2-NG blend, impurities.

NOMENCLATURE

HE	Hydrogen Embrittlement
NG	Natural Gas
SEM	Scanning Electronic Microscope
UTS	Ultimate Tensile Strength
YS	Yield Stress
TE	Total Elongation
R_a	arithmetic Roughness

1. INTRODUCTION

In the last years, many hydrogen production projects from renewable energies (electrolysis, power to gas…) have been submitted to store and transport clean energy. Therefore, to be part of this energy transition, GRTgaz is studying the possibility of using its existing Natural Gas (NG) pipeline grid for the transport of NG-H_2 blend. In order to control the risks of hydrogen transport, it is important to study the interactions between hydrogen and metal, and in particular the impact of hydrogen injection on the mechanical behavior of the pipelines steels, depending on the hydrogen content in the blend. Many works have been published showing that hydrogen decreases the ductility of pipeline steels, initiates cracks on surface and increases the crack propagation rate [1–5]. Besides, these results do not include the NG blend on the damaging effect of hydrogen on the studied material. Only pure hydrogen or a simulated natural gas (N_2) was used. In this study, the effect of the blend H_2-NG has been quantified under 8.5 MPa total pressure with different hydrogen contents. The hydrogen embrittlement has been measured by the quantification of necking at fracture. Moreover, fracture surfaces and cross-section of deformed specimens under hydrogen have been analyzed to provide more understanding on hydrogen embrittlement mechanism.

2. EXPERIMENTAL

2.1 Material

The C-Mn low alloy steel L485-MB (NF EN ISO 3183) was supplied by GRTgaz as a section of pipeline (800 mm nominal diameter and 19.2 mm wall thickness) as shown in Figure 1.a. The L485-MB steel composition is summarized in Table 1.

Table 1: Chemical composition of the L485-MB steel (wt %)

C	Si	Mn	P	S	Al	Cu	Cr	Ni
0.09	0.39	1.61	0.011	0.001	0.38	0.02	0.04	0.03
Mo	**Nb**	**Ti**	**N**	**Fe**				
0.01	0.04	0.02	0.003	Balance				

The nominal mechanical properties of the L485-MB steel were measured at room temperature at $10^{-4}s^{-1}$ strain rate in both Longitudinal (L) and circumferential (C) directions. The Yield Stress (YS), Ultimate Tensile Stress (UTS) and total elongation of the material are presented in Table 2.

Table 2: Nominal mechanical properties of the L485-MB steel at room temperature

Direction	YS (MPa)	UTS (MPa)	Total elongation (%)
Circumferential	558	613	21
Longitudinal	477	593	21

The microstructure of the L485-MB was analyzed in all directions of the pipeline (Figure 1.b). The surface of all specimens were polished mechanically with 800, 1200, 2400 and 4000 grade SiC papers, followed by a 6 µm, 3 µm and 1 µm diamond polishing. Then, the surfaces were observed with an optical microscope (OM) after a 5 sec chemical attack with a Nital 3% solution (3% HNO_3 in ethanol (98%)). The steel microstructure is constituted of ferrite and pearlite. The pearlite is aligned along the longitudinal and circumferential direction caused by initial hot rolling of the plate. Based on image analysis applied to the same plane, the volume fraction of pearlite was estimated to 10-12 %, which is close to the theoretical fraction (12.5%) calculated using the lever rule from a phase diagram obtained by the Thermo-calc™ software.

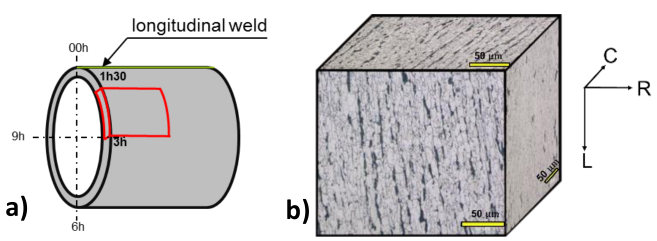


Figure 1: a) Localization of the pipe section of the L485-MB steel, b) microstructure of the L485-MB steel in the Longitudinal (L), Circumferential (C) and Radial (R) directions

2.2 Gaseous tensile test

Tensile tests in high pressure gas were performed on a MTS servo hydraulic testing machine (Figure 2.a) in a dedicated pressure vessel at room temperature. To guarantee the control of the gas content, specifically in terms of impurities, a specific procedure was followed. Several cycles including a primary vacuum followed by filling with nitrogen (N60 purity: 99.9999%) were done. Then, the testing gas is flushed through the system during several minutes. The pressure vessel was then filled with the testing gas to the required pressure (0.2, 2.1 and 8.5 MPa) and the specimen was exposed to the gas during 30 minutes before starting the test to stabilize the temperature and pressure of the vessel. In addition, to measure the load, a dedicated 50kN sensor has been specifically developed. Located inside the pressure vessel, it does not exhibit any signal drift due to hydrogen permeation and circumvents the effect of frictions between the vessel and the loading rod.

In this study, two surface roughnesses (0.5µm and 0.03µm) of the cylindrical smooth tensile specimens have been addressed (Figure 2.b). Moreover, two slow strain rates 10^{-4} s^{-1} and 10^{-6} s^{-1} corresponding respectively to 0.0018 mm/min and 0.18 mm/min displacement rates of the hydraulic cylinder of the testing machine. The specimens were machined in the circumferential direction of the pipeline which corresponds to the highest loading direction in a pipeline under pressure. Yield stress (YS), Ultimate Tensile Stress (UTS), Total Elongation (TE) and Reduction Area (RA) were quantified under different gas conditions (0.2, 2.1 and 8.5 MPa of pure Hydrogen, 8.5 MPa x%H_2-NG mixtures). The tensile tests in different environments have been doubled to confirm the obtained results.

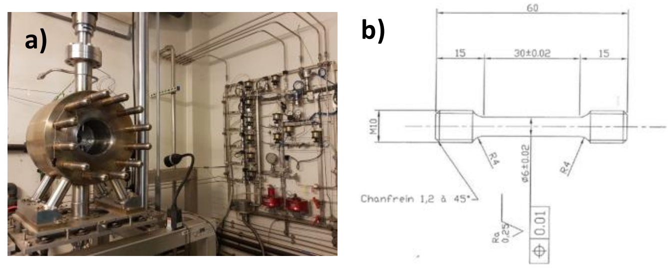


Figure 2: a) MTS servo hydraulic testing machine under high pressure gas, b) geometry of the cylindrical smooth tension specimens

Table 3: Gas compositions used in tensile tests

	100% H_2	2% H_2/GN	25% H_2/GN
H_2	**> 99,9995**	**2,005**	**24,938**
N_2	< 2 ppmv	1,0464	0,7719
CO_2	< 0,05 ppmv	1,0645	0,7836
C_2H_6	-	4,6783	3,4696
C_3H_8	-	0,745	0,5548
C_4H_{10}	-	0,4031	0,3005
CH_4	< 0,1 ppmv	90,057	69,18
H_2O	< 2 ppmv	-	-
THT	-	25,5 mg/m^3	16,7mg/m^3
O_2	< 0,5 ppmv	< 1ppmv	< 1ppmv
H_2S	-	3,87 mg/m^3	2,9 mg/m^3
CO	< 0,05 ppmv	-	-

2.3 Fracture surface observation

The fracture surfaces of the smooths specimens tested in different environments were observed and examined with an optical and scanning electron microscope (SEM). Different regions were identified in function of the partial pressure of hydrogen.

3. RESULTS

3.1 Tensile behavior in high-purity hydrogen gas

Low strain rate tensile tests in high purity hydrogen gas (N55) were performed at room temperature at different pressure of hydrogen (0.2, 2.1, 8.5 and 30 MPa). The main objective is to quantify the embrittlement of the L485-MB steel with the increase of hydrogen pressure. Tensile test curves are plotted in Figure 3 with different experimental conditions. A decrease of elongation at rupture was observed with the increase of hydrogen pressure for both 10^{-4} and 10^{-6} s^{-1} strain rates. The effect of hydrogen was stronger at lower strain rate. However, the tensile test curves indicate that hydrogen has no significant effect on YS and UTS or, if any, the small effect is within the heterogeneity of the material.

The tensile specimens tested in air broke with a classical cup and cone type fracture (Figure 4.a) which corresponds to a large amount of plastic deformation before final failure. Under hydrogen, the fracture mode is changed. A fracture path inclined at 45° from the loading direction was observed (Figure 4.b).

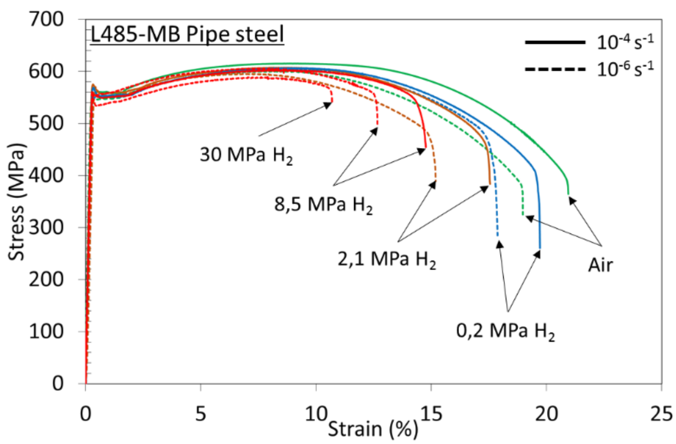


Figure 3: engineering stress (MPa) vs. strain (%) for the L485-MB low alloyed pipe steel in different pressure of high-purity hydrogen gas (N55 : >99.9995%) and ambient air. Two strain rates were used $10^{-4}s^{-1}$ (solid line) and $10^{-6}s^{-1}$ (dashed line)

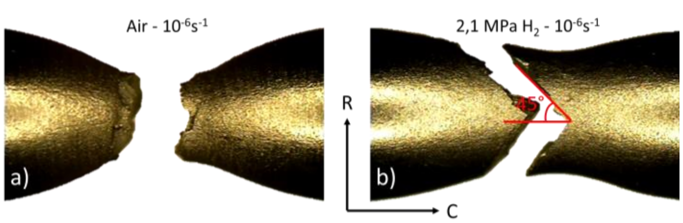


Figure 4: a) Cup and cone fracture mode in ambient air at $10^{-6}s^{-1}$, b) shear fracture mode in 2.1 MPa high-purity hydrogen gas at $10^{-6}s^{-1}$

3.2 Tensile behavior in H_2-NG blends

Tensile tests in NG-H_2 blends were performed at room temperature with several hydrogen contents (0%, 2%, 25% and 100%) at a total pressure of 8.5 MPa (Figure 5). In order to compare with the previous results (Paragraph.3.1), the partial pressure of hydrogen in the blend corresponds approximately to the pressure used for tests in high-purity hydrogen gas.

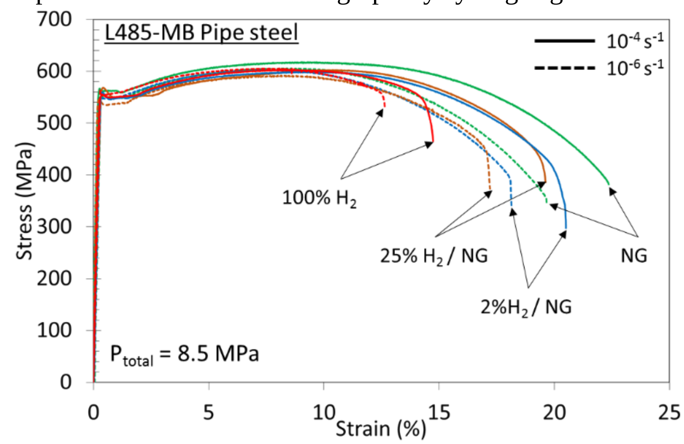


Figure 5: Engineering stress (MPa) vs. strain (%) for the L485-MB low alloyed pipe steel in different %H_2-NG blends at 8.5 MPa total pressure. Two strain rates were used $10^{-4}s^{-1}$ (solid line) and $10^{-6}s^{-1}$ (dashed line)

The results show a decrease of total elongation with the increase of hydrogen content in natural gas (NG) at a given total pressure (8.5 MPa). The loss of ductility in H_2-NG blends shows a similar tendency with the results in pure hydrogen in terms of partial pressure. Besides, these results confirm the effect of strain rate on hydrogen embrittlement: at a lower strain rate, the loss of ductility is greater.

The cup and cone fracture mode was also observed in NG and 2%H_2/NG blend. However, in 25%H_2/NG, a 45° fracture path from the loading direction is observed.

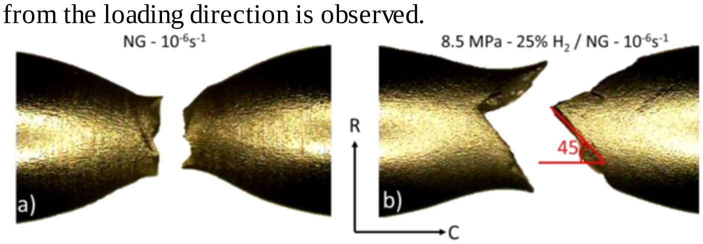


Figure 6: a) Cup and cone fracture mode in Natural Gas (NG) at $10^{-6}s^{-1}$, b) shear fracture mode in 8.5 MPa 25% H_2/NG (corresponding to 2.1 MPa of H_2) at $10^{-6}s^{-1}$

According to Figure 4 and Figure 6, a similarity is observed at the same partial pressure (2.1 MPa) of hydrogen in terms of fracture mode.

Nevertheless, at low partial pressure (~0.2 MPa), the fracture modes are quite different between pure hydrogen and 2%H_2/GN blend as shown in Figure 7.

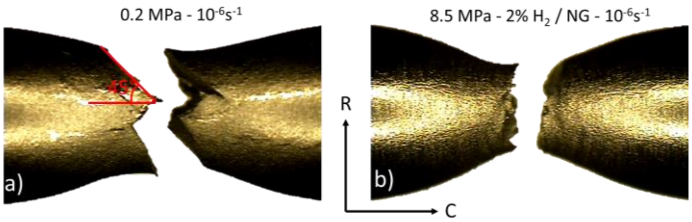


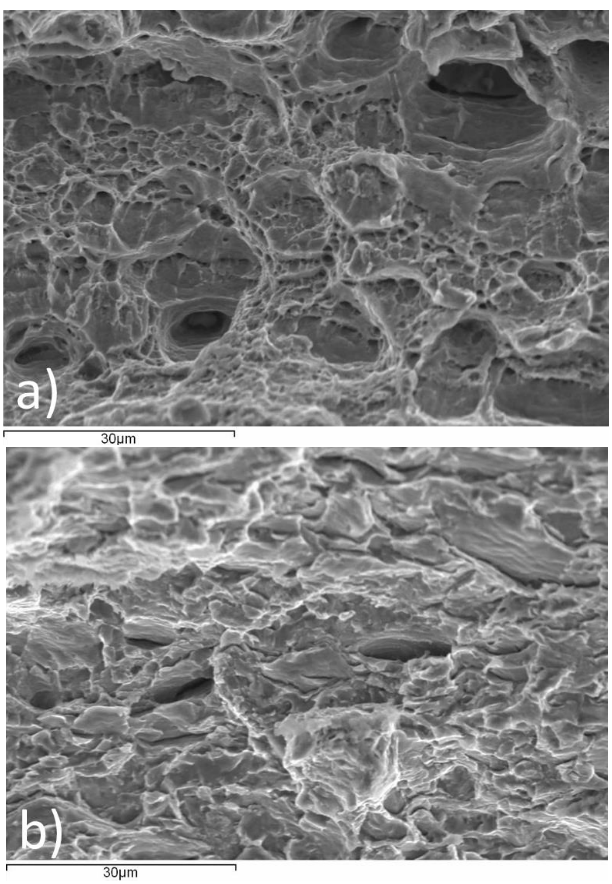
Figure 7: **Fracture mode in a) high-purity hydrogen and b) 2%H_2/NG blend at the same H_2 partial pressure (~0.2 MPa)**

At a sufficient partial pressure (> 2MPa), these results confirm that it is possible to consider the hydrogen partial pressure to evaluate the HE sensitivity of the material. By contrast, at low hydrogen partial pressure and low strain rate, the material behavior is not the same in the blend or in pure hydrogen.

3.3 Fracture surfaces analysis

The fracture surfaces of the tested specimens were observed in a scanning electron microscope (SEM). Three different main areas were identified (Figure 8). The proportion of each area depends on the partial pressure of hydrogen in the gas and on the imposed strain rate.

In ambient air, the dominant feature observed is a classical ductile-dimple type fracture similar to Figure 8.a which corresponds to a high plastic deformation before final failure. The same fracture surface is observed in natural gas and 2% H_2-NG blend (Figure 9.a).



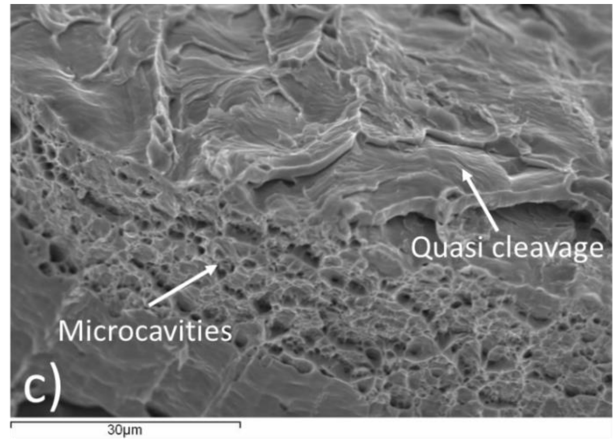


Figure 8: **Fracture surfaces from L485-MB pipeline steel tested at room temperature in 8.5 MPa of 25% H_2-NG blend at $10^{-6}s^{-1}$, a) ductile fracture surface, b) hydrogen affected zone (HAZ) observed in a large area of the fracture surface, c) a mixed zone of quasi cleavage and micro-cavities observed along a pearlite alignment**

By contrast, in high partial pressure (>2.1 MPa) of hydrogen the fracture surfaces change dramatically. A quasi-cleavage type fracture (Figure 8.b) becomes dominant with the presence of delamination along the pearlite planes (Figure 9.b). Moreover, microcavities were observed along delamination which correspond to the ferrite inside the pearlite microstructure (Figure 8.c). Besides, the necking was significantly reduced in high partial pressure of hydrogen compared to NG and air as shown in Figure 9.

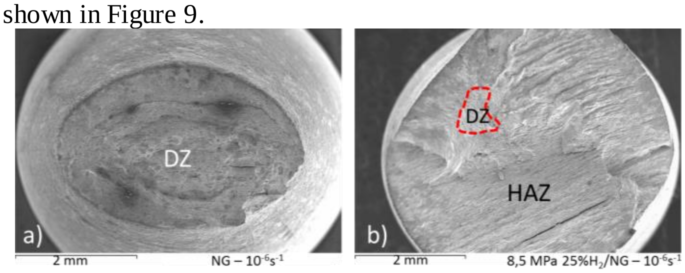


Figure 9: **Fracture surfaces from L485-MB at room temperature in a) Natural Gas (NG) and b) 8.5 MPa 25%H_2/NG blend at $10^{-6}s^{-1}$ strain rate.** ***DZ: Ductile Zone and HAZ: Hydrogen Affected Zone***

3.4 Interrupted tensile tests

Two smooth specimens were loaded up to 4 mm of axial displacement of the hydraulic cylinder corresponding to 13% of total deformation of the cylinder + specimen (Figure 10) at $10^{-6}s^{-1}$ strain rate. The first specimen (blue curve) was deformed in 8.5 MPa high-purity hydrogen followed by a nitrogen purging as indicated by the blue arrow. Whereas the second specimen (red curve) was fully strained in 8.5 MPa high-purity hydrogen.

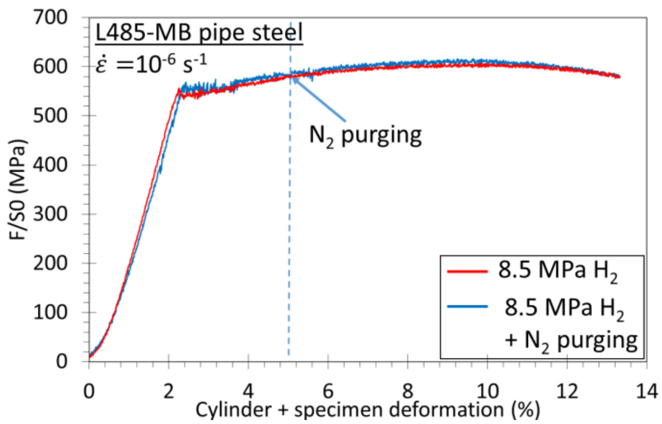


Figure 10: Interrupted tensile test for the L485-MB pipeline steel in 8.5 MPa H_2 (red curve) and 8.5 MPa MPa H_2 followed by a N_2 sweeping (blue curve)

Interrupted tensile test curves in both environment H_2 and H_2/N_2 show a similar mechanical behavior. However, at a finer scale observation of the specimen surfaces, cracks appear only for the specimen deformed completely in H_2 (red curve of Figure 10). SEM observation of the specimen side shows two types of cracks: small cracks (L~10µm) perpendicular to the loading direction (Figure 11-red arrows) and larger cracks (100 µm < L < 2mm) inclined at 45° from the loading direction. Besides, small cavities (D_{cavity} < 100 µm) were observed in the necking zone as shown in Figure 11.

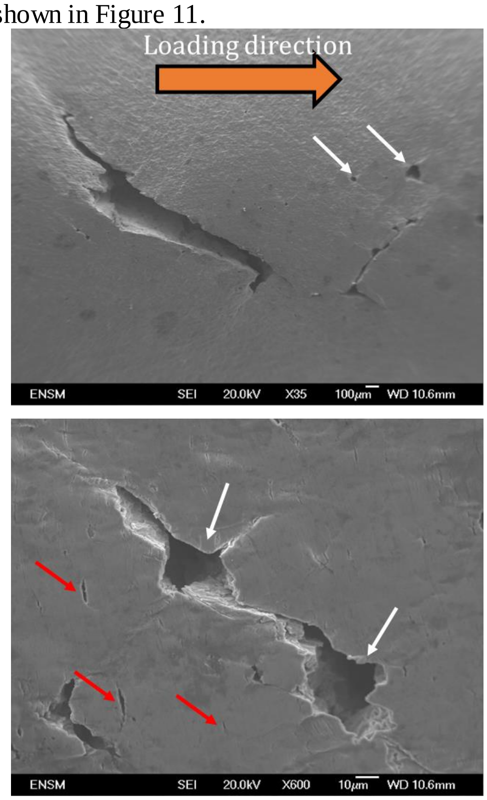


Figure 11: SEM observation of the specimen surface of L485-MB pipeline steel deformed in 8.5 MPa high-purity hydrogen and interrupted in the necking zone. The red arrows indicate the perpendicular cracks and white arrows the observed cavities

4. DISCUSSION

The drop of ductility observed on the L485-MB pipeline steel with the increase of partial pressure of hydrogen in natural gas was consistent with the results of Meng [1]. In his study of the X80 pipeline steel, natural gas was simulated with nitrogen. The author showed a decrease of ductility of smooth specimens with the increase of hydrogen content in N_2/H_2 mixture. The effect of hydrogen was more significant for the notch specimens. Thus, Meng concluded that hydrogen embrittlement (HE) depends on the amount of hydrogen in the bulk of material and the presence of surface defects as cracks promote hydrogen diffusion by dislocation movement.

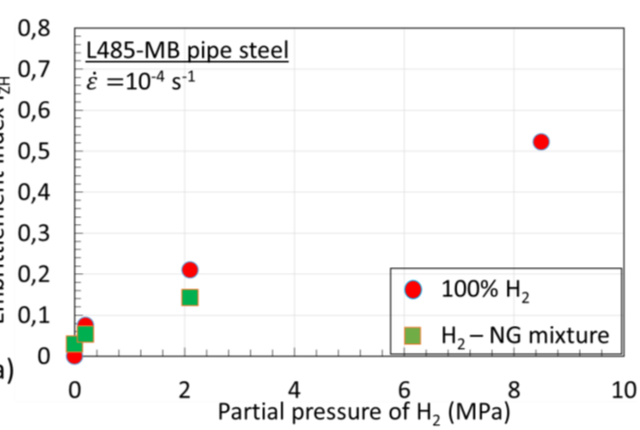
In our study, a composition of natural gas containing impurities was used. The purpose was to investigate the effect of hydrogen content as well as the presence of impurities in H_2/NG mixture on the mechanical properties of the L485-MB pipeline steel. In order to quantify the hydrogen degradation of mechanical properties, an embrittlement index I_{ZH} based on reduction area, defined by the equation (1), was used.

$$I_{ZH} = \frac{Z_{air} - Z_H}{Z_{air}} \quad \text{and} \quad Z = \frac{S_0 - S_F}{S_0} \times 100 \qquad (1)$$

where Z_{air} and Z_H are respectively the reduction of area of the smooth specimens deformed in air and hydrogen, S_0 the initial area of cross section of the specimen and S_F is the minimum area of cross section after failure. When I_{ZH} is null, the material is not susceptible to hydrogen embrittlement (HE), and the embrittlement is maximal when I_{ZH} is equal to 1.

The results expressed in terms of the embrittlement index I_{ZH} are not intended to represent necessarily the true hydrogen service environment for long-term exposure, but rather to provide a practical approach to evaluate quantitatively the severity of hydrogen. H_2-NG mixture

The embrittlement index I_{ZH} in different environment is plotted versus the partial pressure of hydrogen in Figure 12 at $10^{-4}s^{-1}$ and $10^{-6}s^{-1}$ strain rate.

a) 

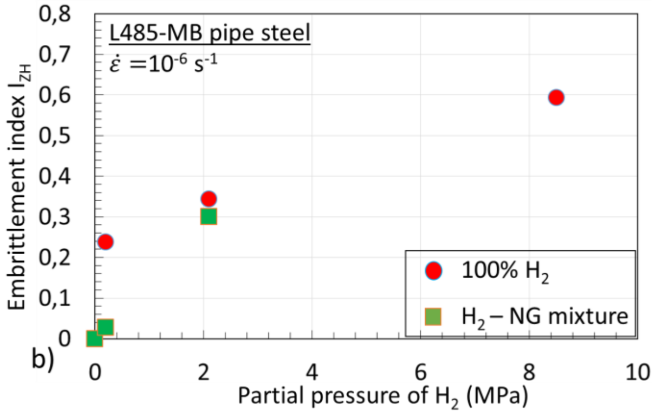


Figure 12: The effect of partial pressure of hydrogen on the embrittlement index I_{ZH} at a) $10^{-4}s^{-1}$ and b) $10^{-6}s^{-1}$ strain rate

The trend in embrittlement index I_{ZH} vs partial pressure in NG/H_2 mixture is similar to pure hydrogen with a slight difference, which correspond probably to the presence of impurities in NG. Otherwise, at low strain rate ($10^{-6}s^{-1}$) and low partial pressure of H_2 (0.2MPa), a significant difference were observed between H_2-NG mixture and high-purity hydrogen, which is also shown in Figure 7. In fact, the presence of impurities at low partial pressure of hydrogen mitigate the effect of H_2 on smooth specimen. Recently, T. T. Nguyen et al. [6] observed that 1% of H_2 in methane with a total pressure of 10MPa has no effect on mechanical properties of the X70 pipeline steel in a gaseous tensile test at $10^{-4}s^{-1}$. Nguyen concluded that 0.1 MPa partial pressure of hydrogen may not be high enough to increase the susceptibility to HE. However, in 0.2 MPa of high-purity hydrogen at a very low strain rate (0.0018mm/min), the L485-MB was susceptible to HE.

In addition, Figure 13 shows the effect of surface roughness on the embrittlement index I_{ZH}. The results indicates that the sensibility to hydrogen embrittlement increases with the surface roughness. It is well known in surface science that surface defects increase the hydrogen adsorption and dissociation [7]. Consequently, a localization of hydrogen in the surface irregularities combined with the high stress concentration in waves may promote crack initiation and lead to premature fracture.

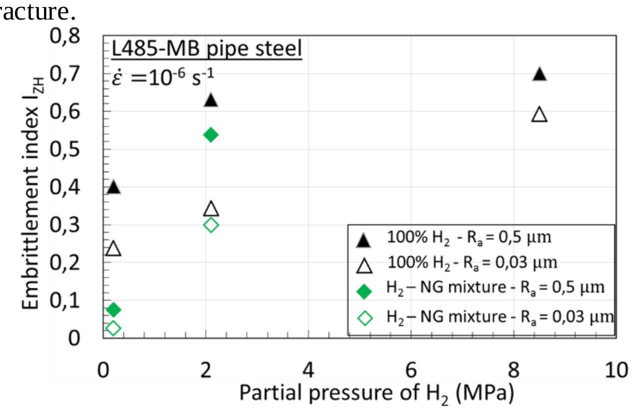


Figure 13: Effect of surface roughness on the embrittlement index of the L485-MB pipeline steel

The analysis of fracture surfaces confirmed the consistence between hydrogen content in NG and partial pressure of hydrogen mainly at higher partial pressure. Two main regions were distinguished on fracture surfaces, a zone characterized by large dimples which corresponds to a ductile fracture, and a zone named "hydrogen affected zone" (HAZ) which corresponds to some quasi-cleavage zones mixed with small dimple areas. The HAZ becomes dominant with the increase of hydrogen partial pressure in NG. Moro et al. observed the same features in the X80 pipeline steel with the increase of hydrogen pressure [2]. However, the L485-MB present a shear type fracture mode oriented at 45 degrees to the loading direction (Figure 14), which is associated to the maximum shear stress, whereas Moro [2] and Nguyen [6] observed a perpendicular fracture to the loading direction. Nevertheless, Kwon et al. observed the same shear type fracture mode of a C-Mn steel (0.17 C, 1.29Mn, 0.31 Si). In his study, hydrogen was introduced electrochemically using a cathodic current density of 2mA/cm² under controlled galvanostatic conditions for 24h at room temperature in a 1 N sulfuric acid solution poisoned with arsenic which is more severe than a gaseous charging [8]. The differences observed in fracture modes may be explained by the microstructure of each material and the severity of charging conditions.

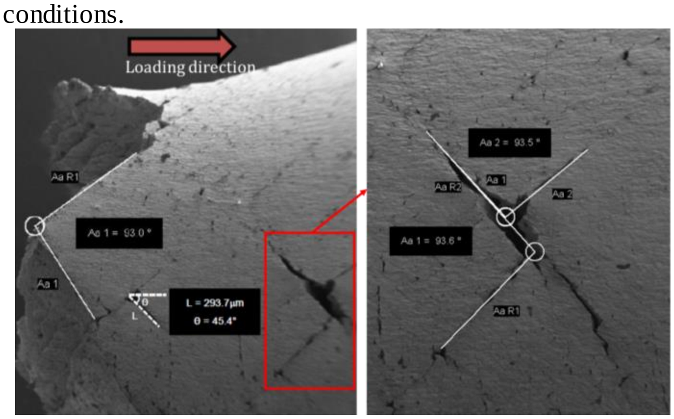


Figure 14: Shear type fracture mode observed on the L485-MB pipeline steel in 2.1 MPa high-purity hydrogen at $10^{-4}s^{-1}$ strain rate

5. CONCLUSION

The susceptibility to HE of the L485-MB pipeline steel was studied and quantified in high-purity hydrogen and NG + H_2 mixtures (0%, 2% and 25% of H_2 mixed with NG). The following conclusions can be made based on our experimental results:

- A drop of ductility is observed with the increase of partial pressure of hydrogen in natural gas. Besides, no significant effect of hydrogen was observed on flow stress. At a partial pressure of hydrogen higher than 2 MPa, the results of tensile tests show a consistency between pure hydrogen and H_2-NG blend.

- A significant effect of surface roughness was observed under hydrogen. the sensibility to hydrogen embrittlement of the L485-MB increases with the surface roughness

- Under tensile loading, there is no effect of 0.2 MPa partial pressure of hydrogen mixed with natural gas on the L485-MB pipeline steel. However, a significant reduction of area was observed in 0.2 MPa of high-purity hydrogen, which may be explained by the effect of the blend to mitigate the effect of hydrogen.

- The L485-MB pipeline steel presents a shear type fracture mode in high partial pressure of hydrogen, whereas a cup and cone type fracture was observed in air, natural gas and low partial pressure of hydrogen in natural gas (0.2MPa H_2).

- Based on interrupted tensile tests, hydrogen induced crack initiation is actuated mainly above the ultimate tensile stress. Cracks appear in the necking zone and oriented at 45 degrees to the loading direction. In air and natural gas, no cracks on the surface were observed.

6. ACKNOWLEDGEMENT

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