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Influence of Hydrogen and Low Temperature on Pipeline Steels Mechanical Behaviour

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Abstract

In the presence of H_2S, metallic materials, such as carbon and low alloy steels, may suffer hydrogen damage and hydrogen embrittlement. Gas transporting pipes in low temperature environment, during the shutdown and the subsequent re-starting operations, are exposed to very low temperatures (T=-40°C). In the presence of high H_2S content in the gas, the risk of brittle failure can be increased due to the effect of hydrogen on steel toughness. In this paper the influence of hydrogen and low temperature on mechanical properties of two pipeline materials, F22 low alloy and X65 micro-alloyed steels, is studied. Steels have been hydrogen charged by means of an electrochemical method: diffusible hydrogen content of steels is in the range 0.6 to 2 ppm. Charpy and J-R curves tests were carried out in the range from room temperature to T=-120°C. Hydrogen affects mechanical properties of the tested materials, mainly reducing fracture toughness in J integral tests, while little influence has been observed in CV tests. Fracture surface examination confirms the results of mechanical testing.

1. Introduction

Carbon steel and low alloy steel are commonly used in Oil and Gas industry when general corrosion due to the presence of CO_2 and H_2S is considered acceptable to stand the design life. However, when sour condition applies, the occurrence of Sulphide Stress Cracking (SSC) in the presence of H_2S on susceptible materials must be investigated [1]. Furthermore, when very low temperatures, as below T=-40 °C, are

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also present, as in most recent oil&gas fields, a synergistic negative effect may result from the combination of sour conditions and low temperatures on the mechanical behaviour of the used materials. Hydrogen charging of steels results in a complex interaction between solute hydrogen atoms and all the micro-structural components in the material. Such a complex correlation causes scatter in the experimental results and sometimes contradictory evidences. Nevertheless, decrease of impact strength, ductility (reduction in area in tensile tests) and fracture toughness of pipeline and pressure vessel steels has been reported in the literature [2][3][4]. Hydrogen can also affect the fatigue limit [5].

To reproduce the combined effect of hydrogen in the metals and low temperature, Charpy toughness and J-integral tests were carried out on specimens charged with hydrogen. Two very "clean" materials produced through a normal commercial production line were used for the purpose.

2. Materials

Experimental activities involved seamless pipes in quenched and tempered conditions manufactured with:

- 2 ¼ Cr 1 Mo steel, ASTM A182 F22 (outside diameter D=320 mm, wall thickness t=65 mm);
- Micro-alloyed C-Mn steel, API 5L X65 grade (D=323 mm, t=46 mm).

The F22 [6] pipe is a Q&T pipe from ingot casting-forging-piercing-hot rolling-quench and tempering production route. X65 [7] grade pipe is a Q&T pipe from conventional billet casting-piercing-hot rolling-quench and tempering operations. Both materials are for sour service use, so that they underwent through all the required qualifications. In Table 1 the chemical compositions of the selected materials are reported. X65 steel microstructure is equiaxed and acicular ferrite with finely dispersed carbides. The microstructure is rather homogeneous. Inclusion shape is round. F22 steel microstructure is typical of tempered lath martensite, i.e., elongated ferrite grains with finely dispersed carbides; the microstructure is rather homogeneous; inclusion density is very low; inclusion shape is round. Mechanical properties have been evaluated at room temperature. Results are collected in Table 2.

Table 1. Chemical compositions

Material	C	Mn	Cr	Mo	Ni	Nb	V	Ti
F22	0.14	0.43	2.25	1.04	0.08	0.023	<0.01	<0.01
X65	0.11	1.18	0.17	0.15	0.42	0.023	0.06	<0.01

Table 2. Mechanical properties

Material	σ_{ys} (MPa)	σ_{ts} (MPa)	E (MPa)	A (%)
F22	468±2.7	592±2.1	206500±1500	20±2.5
X65	511±6.7	609±5.7	206208±6049	21±6.5

3. Experimental procedure

A large number of experimental tests were carried out to characterize the mechanical behaviour of the uncharged and hydrogen charged steels, in terms of:

- Ductile-brittle transition curve, obtained by impact test using standard V notched Charpy specimens;
- Fracture toughness by J-R curves using CT specimens.

A series of specimens were tested uncharged "as received" and a series of specimens were hydrogenated, by the electrochemical method.

3.1. Electrochemical Hydrogen Charging

The electrochemical method proposed for hydrogen charging has the primary purpose to obtain controlled and reproducible charging conditions in an environment that can be prepared, handled and disposed in a simple and safe way. Hydrogen content charged into thick steel specimens should be comparable to that found in pipeline steels after a long service time. The basis for the setup of the hydrogen charging method was the work of Newman and Shreir [9]. The procedure finally setup in our laboratories for electrochemical hydrogen charging has been:

- Solution: 0.4 mol L^{-1} of CH_3COOH + 0.2 mol L^{-1} of CH_3COONa, buffered at pH 4.3 and with 600 ppm of sulfide as S$^=$ from hydrated sodium sulfide
- complete de-oxygenation with pure N_2
- room temperature, T = 25 ± 3 °C
- current density equal to 0.5 mA/cm^2 for 20 hours

In order to avoid hydrogen release due to diffusion during the time interval from charging to mechanical testing the charged specimens were immerged into liquid nitrogen at T=-196 °C or coated with FCC metals (Ni and Cu).

An approximate estimation of the diffusible hydrogen content of the charged specimens has been made by using the hot glycerol method. This method is very simple and quick, then it is suitable for a routine control but underestimate the actual hydrogen content. A control measurement of the total hydrogen content was performed in external laboratories, using a commercial LECO hydrogen analyser. The two methodologies were in general agreement; diffusible hydrogen content of the charged specimens is in the range 0.6-2 ppm. The details of the experiments are reported in the paper [10].

3.2. Charpy tests

Charpy tests were carried out on as received materials and after hydrogenation, according to ISO 148 [11]. The specimens were cooled down, by an ethanol-liquid nitrogen bath kept at the test temperature. Two methods were followed to define the brittle-ductile transition temperature (BDTT): by the fracture appearance transition temperature (FATT) and by determining the temperature in correspondence of the energy equal to 27J. The FATT is typically defined as the temperature at which the fracture surface contains the 50% of brittle area.

3.3. Fracture mechanics tests

Fracture mechanics tests were carried out on standard CT specimens, following the ASTM 1820 [12]. Thickness of the specimen is a very important parameter for the test. Large thickness is needed to have a plane strain behavior of the material, on the other hand small thickness allows easier and faster charging processes that depend on the surface/volume ratio. In designing the specimen both those requirements were taken into account and thickness was set equal to B=20mm. Side grooves were machined on the specimens, along the crack propagation direction, in order to reduce the plane stress condition. The tests have been performed at different controlled temperatures by using an environmental chamber fed with liquid nitrogen. To check the specimen temperature in the bulk, before and during tests, a small hole was machined in the specimens and a T-type thermocouple was welded in, without interfering with the test. The details of the experiments are reported in the paper [8]. All the specimens, after the hydrogen charge, were maintained in liquid nitrogen, while some specimens were kept in air at room temperature for 24h to allow some diffusible hydrogen to escape from the specimen and verify if there is a permanent effect of hydrogen charge.

4. Results and discussions

The effect of the hydrogen charge is evident both for F22 and X65 steels, and this effect is particularly evident in the slower J-integral tests.

4.1. Charpy tests

Figs. 1 and 2 show the Charpy impact energy values and the percentage of brittle area as a function of temperature for F22 and X65 steel respectively. The impact energy values of uncharged F22 specimens are almost constant to a temperature equal to T=-100°C (see Fig. 1a). The same results are achieved from the percentage of brittle area diagram (see Fig. 1b): the brittle area is between 5-10%, when test temperature is equal to T=-100°C. The energy values drop suddenly in correspondence of T=-110°C. The transition zone of impact energy of hydrogenated specimens is larger and the energy values are more scattered. The BDTT of hydrogenated F22 specimens increases of about 30°C with respect of the non-hydrogenated specimens, if it is considered the value in correspondence of impact energy 27J, as in ISO148. By considering, on the contrary, the FATT value the increase is in the range of 20°C. Upper shelf energy is slightly decreased from 270 to 230 J.
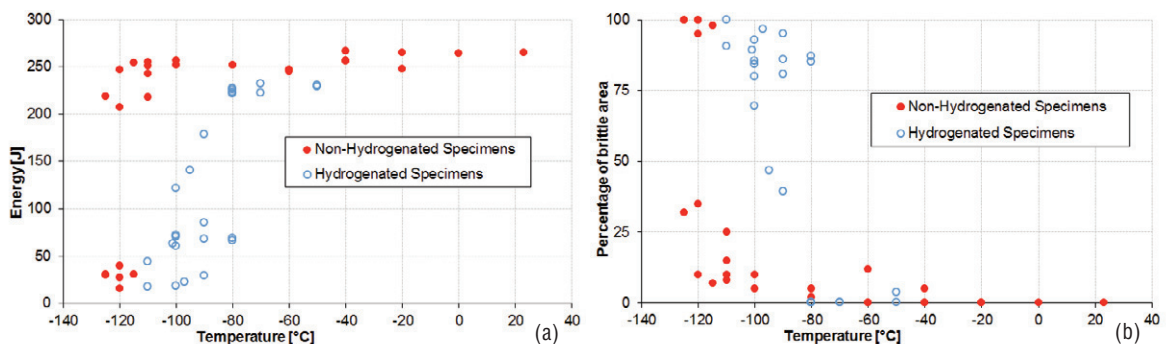

Fig. 1. (a) Impact energy and (b) percentage of brittle area vs. temperature for non-hydrogenated and hydrogenated F22 steel
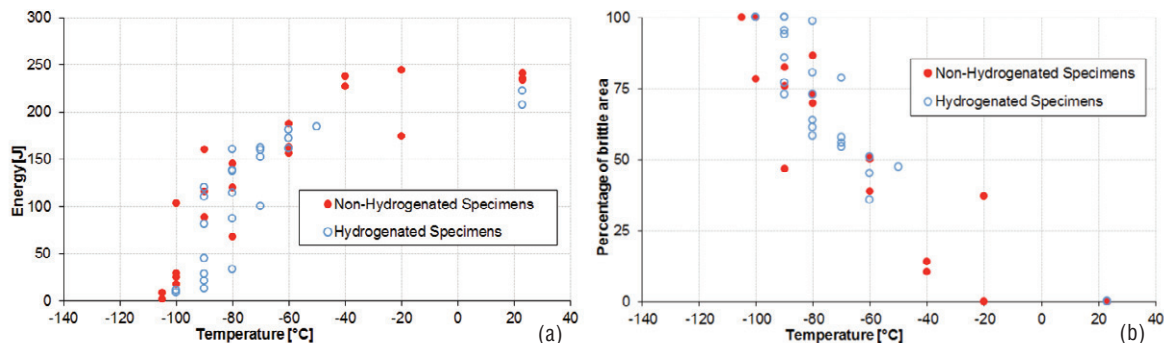
Fig. 2. (a) Impact energy and (b) percentage of brittle area vs. temperature for non-hydrogenated and hydrogenated X65 steel

X65 steel hydrogenated specimens show a slightly different behaviour, if compared to the uncharged material one. The transition was a bit more localized. An increase of BDTT of about 10°C can be appreciated after hydrogenation, using both the FATT and the 27J criterion. The upper shelf energy is slightly decreased from 240 to 220J. An important aspect is the more scattered results for both energy and brittle area values of hydrogenated samples compared to those of uncharged material. Results indicated that both F22 and X65 steel behave in a similar way and in all cases a slight increase of the transition temperature was found.

4.2. J-integral tests

Fig. 3(a) and 3(b) shows the measured values of J_Q, vs. temperature for F22 steel and X65 steel respectively, with and without hydrogen.

The effect of the hydrogen charge is more evident if the toughness fracture J-R curves are considered. When material is charged with hydrogen, in fact, J_Q values decrease significantly in both steels with respect to the values obtained in the uncharged conditions. Fig. 3 shows the J_Q values obtained by non-hydrogenated F22 specimens: the values are larger than 900 kJ/m^2 at a temperature of T=-100°C. During the tests the cracks never propagate in an unstable way and also the stable crack propagation is very small. The plastic zone at the crack tip is large and the crack tip blunts without propagation. The J_Q values obtained by the hydrogenated specimens are significantly lower and almost constant ($J_Q \approx 150$ kJ/m^2) to the room temperature. Fig. 4(a) shows the J_Q values divided in the elastic, J_{el}, and plastic, J_{pl}, components: it is evident that the elastic component is almost constant; on the contrary, the presence of hydrogen drastically reduces the plastic one. The presence of hydrogen modifies the fracture mode of the material: the plastic zone is smaller and the crack propagation is larger.

In Fig. 5 the fracture surfaces of F22 specimens are shown. During the tests the cracks, in both specimens, did not propagate in an unstable way. The specimens were heat-tinted in order to mark the stable crack propagation phase, which is visible on the crack surfaces. It is possible to notice that the stable propagation of the non-hydrogenated specimen at T=-100°C is clearly lower than the values found in the hydrogenated specimen at T=-90°C.

Some specimens (green symbols) were kept in air at room temperature before the J tests: it is evident that, even in this case, the J_Q values are lower than the ones of the non-hydrogenated specimens. The aim of these last tests is to put in evidence the role played by the presence of trapped hydrogen in the lattice.

As a matter of fact we can expect that large amount of diffusible hydrogen can escape from the specimen in 24 hours being this time almost the same of the charging one, that is equal to 20 hours.

Similar considerations are valid for X65 steel: Fig. 3(b) shows that the J_Q values of the hydrogenated specimens are significantly lower the non-hydrogenated ones and are almost constant ($J_Q \approx 90$ kJ/m^2) with the temperature. Fig. 4(b) shows the J_Q values divided in elastic and plastic components: the presence of hydrogen prevents the plasticization of the material.
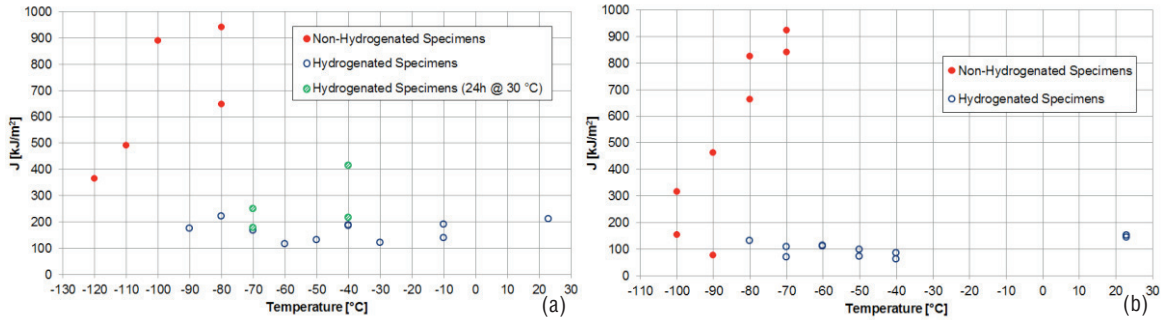
Fig. 3. J_Q values obtained by non-hydrogenated and hydrogenated specimens of F22 (a) steel and X65 (b)
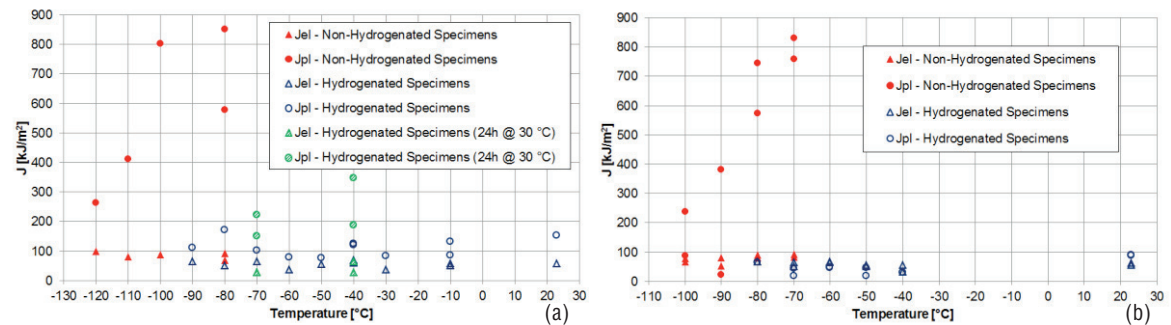

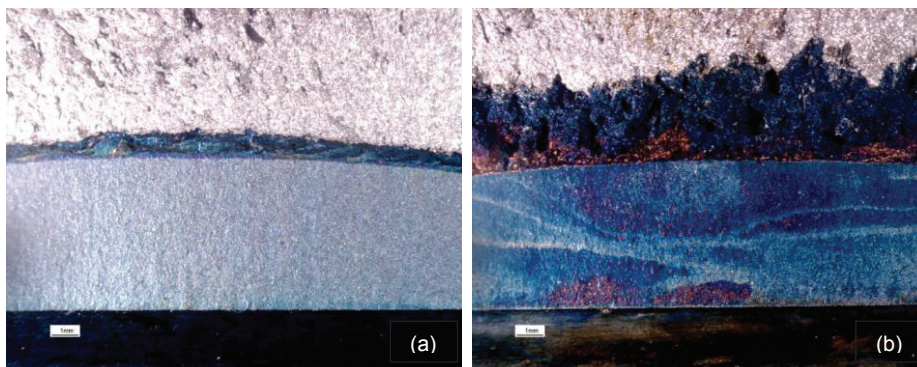Fig. 4. Jel and Jpl components obtained by non-hydrogenated and hydrogenated specimens of F22 steel (a) and X65 (b).

Fig. 5. Stable crack propagation for F22 specimens: (a) uncharged specimen, T = -100°C, J_Q = 890 KJ/m^2, Δa = 0.5mm; (b) Charged specimen, T = -90 °C, J_q = 179 kJ/m^2, Δa = 2.5 mm

4.3. Fracture surface examination

In Fig. 6 the behaviour of X65 steel without hydrogen is shown: fatigue crack growth, crack tip blunting, ductile crack extension and unstable crack propagation are visible. Ductile crack extension generally is not uniform along the fatigue crack tip and sometimes is a little more extended near the edges where stress triaxiality is lower even in the presence of side groves. Ductile fracture exhibits ductile dimples nucleated by inclusions or precipitates. Finally unstable crack propagation shows typical aspect of transgranular cleavage, with secondary cracks transverse to the primary fracture. Inclusions don't have any effect on brittle fracture nucleation even when they can be occasionally found on the fracture surface.

In the hydrogen charged specimen, the stable crack growth stage has a "cellular" morphology which, at low magnification, is similar to an intergranular fracture, see Fig. 7(a), but actually it is due to a mixed fracture mechanism, i.e., a brittle mode in the central part of each cell and a ductile mode on the border.

This kind of brittle mode can be called "quasi-cleavage" because, in contrast with pure cleavage, it is very often nucleated by inclusions, Fig. 7(b). The dimension of these cells can be reasonably estimated in the range 30÷125 μm, much larger than the ferritic grain size that is in the order of few microns. The ductile component of the stable fracture forms a continuous net which gives to the fracture the "cellular" appearance and absorbs most of the fracture energy in this stage, much lower than the one of pure ductile fracture. Finally unstable crack propagation shows the typical cleavage mode without significant differences respect to not hydrogenated specimens.
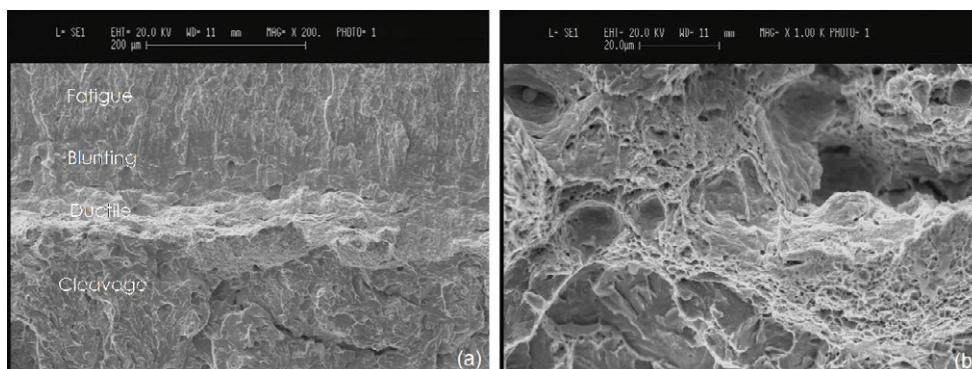

Fig. 6. Fractographic analysis of X65 specimen without hydrogen after J integral test
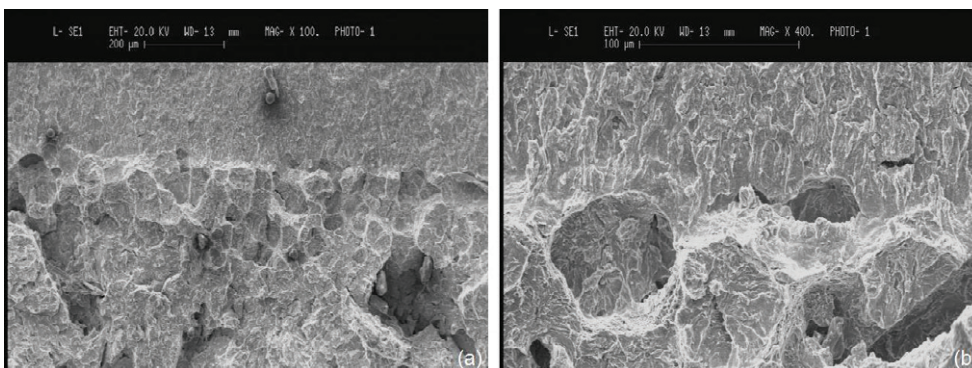

Fig. 7. Fractographic analysis of X65 specimen charged with hydrogen after J integral test.

In specimens without hydrogen, F22 steel has a more extended blunting and it appears very flat. Ductile crack extension shows very big and flat dimples surrounded by small ones not well developed. Fracture surface of hydrogenated specimens of F22 steel displays the same general morphology of X65 with some differences: the surface ratio of ductile to "quasicleavage" fracture is higher, i.e., the ductile component of the fracture is higher, thus justifying the higher toughness of F22; on the other hand the mean dimension of the cells is in the range 35÷150 μm, slightly higher than the one measured on X65.

5. Conclusions

In this paper, the mechanical behavior of two hydrogenated steels was investigated. Both steels, a forged low alloy steel named F22 and a microalloyed steel named X65, are widely used in oil&gas pipelines. The conclusions can be summarized as follows:

- An electrochemical hydrogen charging technique was developed; hydrogen content in the specimens was measured between $0.6 \div 2$ ppm; hydrogen diffusion outside the specimen was prevented by means of putting specimens in liquid nitrogen or coating with FCC metal.
- A suitable procedure was applied for testing of hydrogen charged specimens in order to obtain mechanical parameters such as: Charpy impact energy and toughness varying test temperature from room temperature to - 120°C, without any remarkable hydrogen loss in the material.
- A drastic change in mechanical properties of the hydrogenated material has been shown; the effect, as expected, was remarkable in those tests that require a longer time to be performed, such as J integral tests and lower in fast fracturing impact tests.
- The characteristic toughness value, J_Q, shows an evident loss in mechanical performances if compared to the uncharged one. In particular the material loses the ability to plasticize under high loads and stresses and its behaviour shifts to those of medium tough steels.
- Hydrogen effect is not temperature dependent and J_Q values, experimentally obtained from charged specimens, are very similar while varying test temperature: for F22 steel $J_Q \approx 150$ kJ/m^2 and for X65 steel $J_Q \approx 90$ kJ/m^2; these values, even if largely influenced by the hydrogen, are always sufficiently high.
- The morphology of fracture surfaces was influenced by the hydrogen charging: the stable crack growth stage has a "cellular" morphology which is due to a mixed fracture mechanism, i.e., a hydrogen induced brittle mode in the central part of each cell and a ductile mode on the border.
- Toughness reduction was noticed also on specimens that have been left at room temperature and open environment for 24h after hydrogen charging, to allow hydrogen diffusion outside the specimen. It resulted clear then, that a certain amount of hydrogen introduced in the specimens was trapped inside the material.

Acknowledgements

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