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Procedia Structural Integrity 42 (2022) 977–984

Structural Integrity Procedia

www.elsevier.com/locate/procedia

23rd European Conference on Fracture - ECF23

Effect of hydrogen charging on Charpy impact toughness of an X70 pipeline steel

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Abstract

Hydrogen uptake in steel structures can cause a degradation in mechanical properties such as toughness, and can induce cracks. This phenomenon is widely known as hydrogen embrittlement. For structural steels subjected to cathodic protection or pipelines transporting high-pressure hydrogen gas, hydrogen embrittlement represents an important challenge. Charpy V-notch testing provides a fast and inexpensive method for quantifying the impact toughness of a steel. However, its validity for assessing hydrogen embrittlement is uncertain. In this work, the influence of hydrogen uptake on the impact toughness of an API 5L X70 pipeline steel is investigated. Charpy V-notch impact tests are performed in air, both uncharged and after electrochemical hydrogen pre-charging. Different charging times are used, and the influence of hydrogen-induced cracking is studied. The temperature range of the Charpy impact tests is between -80 °C and +20 °C. A rising upper shelf phenomenon is observed in the uncharged specimens and the ductile-to-brittle transition temperature (DBTT) is not reached for the tested temperatures. For this material, hydrogen uptake causes a reduction in Charpy impact energy at the higher test temperatures, with the highest reduction measured at room temperature. A post-mortem analysis of the fracture surfaces suggests that the presence of hydrogen in the lattice aids the formation of separations during fracture, lowering the absorbed energy.

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10.1016/j.prostr.2022.12.123

Keywords: Hydrogen embrittlement; Pipeline steels; Charpy V-notch; Impact toughness; Fractography

1. Introduction

Hydrogen gas will play an important role in the storage and transport of energy (produced by renewable sources or in conjunction with carbon capture and storage). From an economic standpoint, existing pipeline systems are an attractive infrastructure for transporting and distributing hydrogen gas. However, hydrogen entry into pipeline steels can cause a degradation in mechanical properties, generally referred to as hydrogen embrittlement (HE). Since present pipelines were not designed for high-pressure hydrogen transport, their suitability must be checked (Laureys et al. (2022)). Charpy impact testing is easy, cheap, and widely used to qualify the toughness of pipeline steels and their welds. This makes the test an attractive option for the qualification of hydrogen embrittlement or the impact toughness of a material in hydrogen charged conditions. However, it is unclear whether the results properly reflect the interaction of hydrogen with the material under practical circumstances. Hydrogen embrittlement severity depends not only on material properties and microstructure, but also on the type of test and the testing conditions. It is, for example, often reported that the degree of hydrogen embrittlement in tensile tests depends on the strain rate (Depover et al. (2016)). Since Charpy impact testing is a dynamic test, the time for hydrogen diffusion during the test is very limited. This high strain rate might make Charpy impact testing inappropriate for hydrogen embrittlement evaluation (Nagumo (2016)). Still, some authors have reported a change in ductile to brittle transition temperature (DBTT), and in impact energy when performing Charpy tests on hydrogen charged specimens. Fassina et al. (2012) tested two pipeline materials, an API 5L X65 and an ASTM A 182 F22 steel. They reported a diffusible hydrogen content of 0.6 – 2 ppm and found an increase in the DBTT and a decrease in upper shelf energy (USE) due to hydrogen for both steels. Additionally, the scatter on the results of the hydrogen-charged samples was larger. They observed no difference in fracture surface appearance. Mori et al. (2015) found that the Charpy impact energy of 4340 steel tempered at temperatures above 468°C was affected. Rosenberg and Sinaiova (2017) found no influence on the Charpy impact energy values after hydrogen charging an API 5L X70 pipeline steel as well as an S355 structural steel, although a higher scatter for hydrogen charged specimens was also reported. However, after subjecting the specimens to a static preload for 24h, allowing hydrogen to diffuse to the notch tip, they did note an influence on the upper shelf energy and the DBTT. Golisch et al. (2022) investigated base metal and weld specimens of a spiral welded grade L415ME steel pipe. They reported a diffusible hydrogen content of 3.43 ppm and 3.75 ppm for base metal and weld, respectively, and observed a significant reduction in CVN impact energy. The reduction in impact energy found by Golisch et al. (2022) (about 84 J to 99 J) was more than double the one seen by Fassina et al. (2012), who found the USE decreased about 20 J and 40 J for the X65 and F22 steel, respectively. This is possibly related to the difference in hydrogen content between the two studies, or the different materials studied. Previously mentioned authors all used electrochemical methods to charge the samples with hydrogen. In the present work, the influence of electrochemical hydrogen charging on the Charpy impact energy of an API 5L X70 pipeline steel is characterized.

2. Materials and methods

The tested material is an API 5L X70 steel, produced in 1991. Specimens were extracted from the mid-thickness region of a pipe with diameter 1016 mm (40”) and wall thickness 15.8 mm that had been previously in service in a natural gas pipeline. Standard Charpy V-notch specimens (10 mm x 10 mm cross section) were machined according to EN-ISO 148-1 (International Organisation for Standardization (2016)), and had a longitudinal-transverse (L-T) orientation. Impact tests were performed for temperatures ranging from -80 °C to 20°C in steps of 20 °C. The specimens were cooled in a cooling bath at the testing temperature for 5 min, and the time between removing the specimen from the bath and the striking of the hammer was no more than 5 s. For hydrogen charged specimens, the time between the end of charging and submerging into the cooling bath was minimized and never exceeded 1 min. Specimens that were not fully fractured during the test were submerged in liquid N_2 and broken in order to examine the fracture surface.

Hydrogen charging was done electrochemically using a 0.5 M H_2SO_4 electrolyte with 1g/L thiourea (CH_4N_2S) added as a hydrogen recombination poison. A constant current density of 0.8 mA/cm^2 was applied. Table 1 gives the measured total hydrogen content for the two hydrogen charged conditions. This total hydrogen content was measured for 10 x 10 x 10 mm^3 cubes extracted from the center of the pipe, using hot extraction at 900 °C (Galileo G8), with a minimum of three repeat tests for each condition and 1 min waiting time between the end of charging and the start of the measurement. No hydrogen-induced cracking (HIC) due to the charging procedure was found in Charpy specimens charged for 8h, but after 48h hydrogen charging some fine HICs could be found in the mid-thickness region of the specimens. An example of such cracks is shown on Fig. 1. This condition will serve to verify whether hydrogen-induced damage in the form of cracks (HICs) affect the Charpy results. The HIC found in this material was previously discussed by Cauwels et al. (2022). At 48h charging, the Charpy specimen is close to saturation, while at 8h the specimen is not yet saturated with hydrogen.

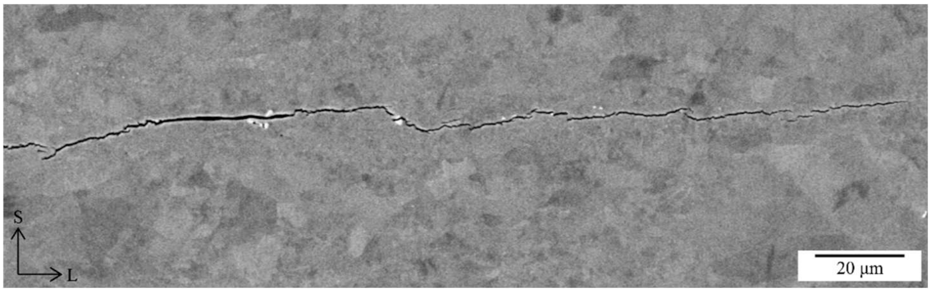

Fig. 1. SEM image of a hydrogen-induced crack in the X70 steel

Table 1. Overview of the tested hydrogen charged conditions and associated hydrogen content

Material	Electrolyte	Current density (mA/cm^2)	Charging time (h)	H content (wppm)
X70	H_2SO_4	0.8	8	0.98 ± 0.09
X70	H_2SO_4	0.8	48	1.29 ± 0.44

3. Results and discussion

Fig. 2 shows the measured impact energies both in air and the two different hydrogen charging conditions. The transition temperature was not reached within the tested temperature range since all samples (including all tested temperatures and hydrogen charging conditions) exhibited 100% shear area.

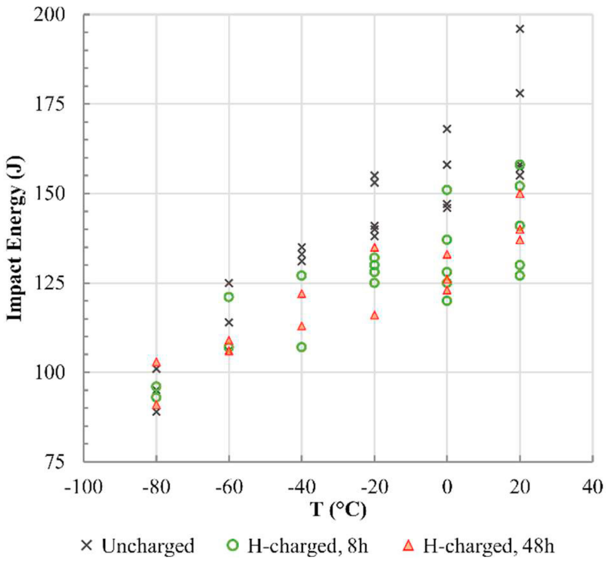

Fig. 2. Charpy impact energy values measured for X70, tested in air and with different hydrogen-charged conditions

Since the DBTT was not reached in this test series, no conclusions can be drawn as to the effect of hydrogen on it. On Fig. 2, it can however be seen that hydrogen charging did influence the Charpy impact energy of the X70 specimens, though only for the higher test temperatures. From Fig. 2, a difference between air and hydrogen tests can be seen from room temperature down to and including -40°C. A Student t-test for equality of averages was performed to check the significance of the observed differences. For temperatures of 0 °C and 20 °C, the decrease in impact toughness compared to air was statistically significant for $p < 0.05$. For -20 °C, the difference was significant for 8h charged samples but not for 48h charged samples. The effect of hydrogen could also be seen to diminish with decreasing temperature. At room temperature, an average drop of about 16% in impact energy could be observed after hydrogen charging for 8h, while at -20°C the decrease in impact energy was about 12%. The scatter on the hydrogen charged specimens also appears to be more pronounced than for uncharged samples, as similarly observed in literature, e.g. by Fassina et al. (2012).

Rather than showing a constant upper shelf energy value, the impact energy steadily increases with higher temperatures. This phenomenon is called a rising upper-shelf (RUS), and is associated with control-rolled pipeline steels that fracture with the formation of separations, also called splits or delamination cracks (Davis (2017)). Separations can indeed be seen on the fracture surfaces, parallel to the crack propagation direction. Fig. 3 depicts some fracture surfaces of Charpy specimens tested at 20°C, -20°C and -80°C.

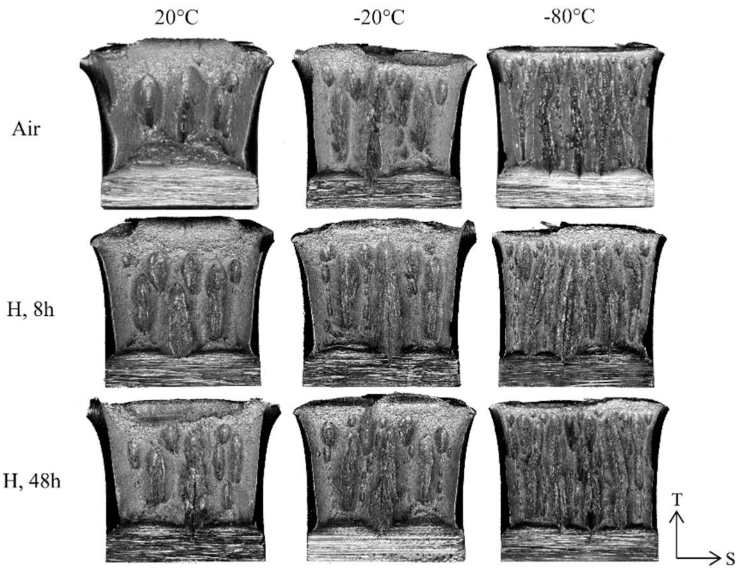

Fig. 3. Optical microscopy images of selected fracture surfaces of Charpy specimens

The observed splits can be classified as a ‘crack-divider’ type, which is typical for L-T oriented specimens (Arnoult et al. (2015)). The cause of separations has been attributed to different properties of the steel: (i) composition, e.g. high S and P content, (ii) microstructure, e.g. microstructural banding, elongated ferrite grains, ferrite-pearlite banded microstructures and/or coarse ferrite grains and (iii) texture, e.g. cube fiber textures or microstructural bands with different crystallography (Davis (2017); Haskel et al. (2014)). The microstructure of the investigated X70 pipeline steel has been previously discussed in more detail by Cauwels et al. (2022), and contains several of aforementioned causes for separations, including the ferrite-pearlite banded microstructure and a pronounced plastic anisotropy. Separations then occur when the stresses in the through-thickness (S) direction, arising from the stress concentration at the notch, are sufficiently high to delaminate the anisotropic microstructure of the steel along weak paths (Arnoult et al. (2015)). With increasing temperature, the severity of the observed separations decreases and the measured impact energy increases. When a crack-divider separation occurs, it splits the fracture surface apart, effectively reducing the local thickness of the specimen and lowering the through-thickness constraint. This, in turn, reduces the energy absorbed during the test. The influence on the impact toughness is strongly linked to the moment the separation happens in the fracture process. The earlier a separation occurs, the more significant the reduction in absorbed energy, as more of the fracture process will be governed by a partitioned stress state (Ruggieri and Hippert (2015)). The separation can also sometimes be seen to run into the notch of the specimen, called ‘notch breach’. For the tested material, only very few of the tested samples did not show notch breach. The samples without notch breach consistently showed the highest impact energy values within their temperature-condition set. For example on Fig. 3, the sample tested at room temperature in uncharged condition had no notch breach.

Comparing uncharged and charged specimens in Fig. 3, the number of splits on the fracture surface increased for the hydrogen charged specimens. The severity of separations on the fracture surface can be quantified in different ways. Sugie et al. (1983) defined the separation index (SI) as the ratio of the length of all separations to the inspected fracture surface area. For specimens tested at the same temperature (and above -20 °C), hydrogen charged samples generally had a higher SI. Fig. 4 plots the separation index for all specimens against their impact energy. A higher SI is clearly associated with a lower Charpy impact energy. Since a higher separation severity can be linked to a decrease in impact energy, the effect of hydrogen on impact toughness could be partially attributed to the increased separations occurring in hydrogen-charged specimens. Farber et al. (2015) argued that rather than the number or length of separations, the length of the ductile crack zone is a more relevant factor for the absorbed energy. Separations that cross into the notch also subdivide this zone and the occurrence of early delamination could contribute to reducing its size. Since Charpy impact tests are dynamic, there is little to no time for hydrogen diffusion and redistribution during the test. Hydrogen embrittlement mechanisms that rely on hydrogen diffusing to the highly stressed regions in front of a notch or growing crack are probably much less likely to be activated in the Charpy test. According to the hydrogen enhanced decohesion mechanism (HEDE), hydrogen can weaken interatomic bonds, thus promoting decohesion. Solute hydrogen can either occupy lattice sites, or segregate towards and accumulate at defects in the microstructure, so-called hydrogen traps. These traps include, among others, dislocations, inclusion/matrix interfaces, high-angle grain boundaries and ferrite/pearlite interfaces. In other words, hydrogen can accumulate at the grain boundary of elongated grains, or ferrite-pearlite interfaces, which were above mentioned to be critical for separations. The presence of hydrogen may then decrease the though-thickness stress required to trigger a delamination by weakening the interfaces or boundaries where the separation occurs. This hydrogen-related promotion of separations or delaminations was also seen by Moro et al. (2010) in an X80 pipeline steel.

The vanishing influence of hydrogen at lower temperatures could be related to two points. First, the through-thickness (S direction) stress level in the Charpy specimen increases with lower temperatures due to an increase in the yield strength. This could indicate that the through-thickness stress level is already sufficiently above the critical value for delamination, even without hydrogen, and that any additional lowering of the threshold for separation is comparatively less pronounced. In other words, a further reduction in impact energy by increased splitting becomes less viable as temperature decreases. Secondly, hydrogen may influence the measured Charpy impact energy in a different way than by increasing separations. In their Charpy tests on S355 steel, Rosenberg and Sinaiova (2017) observed a reduction in plastic zone size for hydrogen charged (and preloaded) specimens compared to uncharged specimens as well as a fracture mechanism change from ductile dimples to quasi-cleavage and mentioned the hydrogen-enhanced strain-induced vacancy (HESIV) model as possibly at play. Mori et al. (2015) argued that hydrogen atmospheres might be transported by dislocations to the fracture site, at faster rates than lattice diffusion rates, which caused the observed change in impact energy. The interaction between hydrogen and dislocations would more likely play a role at room temperature than at -80 °C, where the mobility of both is much reduced.

It should be noted that, because the dwelling time in the bath is kept constant, slight variations in hydrogen content at the moment of the hammer strike are possible. At higher temperatures, the diffusion of hydrogen will be faster, meaning more hydrogen can effuse out of the specimen during the cooling at higher bath temperatures, but hydrogen can also redistribute within the specimen At lower temperatures, however, there will also be less hydrogen loss but also less redistribution of hydrogen throughout the specimen during the waiting time. This redistribution may be more important for the 8h charged specimen, which is not fully saturated, and where some of the hydrogen can diffuse towards the center. Because of the relative difference in timescale between the pre-charging time and the waiting time, however, the variation in hydrogen content was not expected to play an important role.

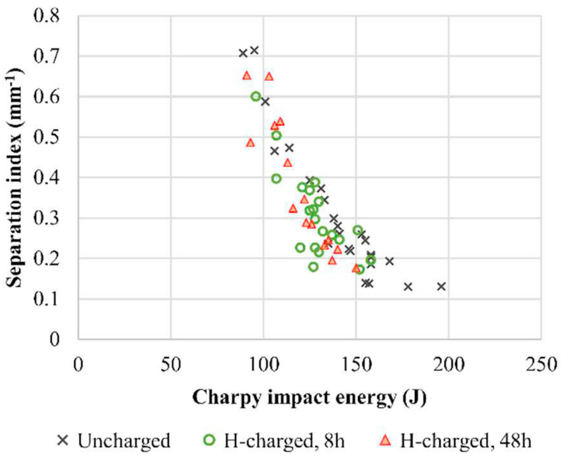

Fig. 4. Separation index (SI) plotted as a function of impact energy for different hydrogen charged conditions

To evaluate the potential role of HICs on the Charpy impact energy, specimens charged for 8h and 48h in the acid electrolyte were compared and little difference was obtained (cf. Fig. 2). The minor difference in impact energy was also found to be statistically insignificant for all temperatures. Part of the reason for this observation may be that the difference in hydrogen content between these two conditions was limited (cf. Table 1), or that the effect of hydrogen is not simply scalable for this type of test and material. Furthermore, the presence of hydrogen-induced cracks in the 48h specimens did not seem to influence impact toughness. A similar conclusion was reached by Hardie et al. (2006), where hydrogen-induced cracks originating from the charging did not influence the tensile curve after the hydrogen had desorbed. It is also possible, given the rather arbitrary nature of the hydrogen-induced cracks, that they did not form sufficiently close to the notch to influence the Charpy test. As it turns out, the results indicate that even for electrochemical charging conditions that are severe enough to induce some cracks, the effect on impact toughness is a result of the hydrogen in the sample, and not the presence of cracks during this type of testing. To further confirm this, three Charpy specimens were charged for 48h and three for 8h and then left for up to one week in a vacuum chamber to allow for hydrogen desorption. Afterwards the specimens were Charpy tested at room temperature, where the largest effect of hydrogen on Charpy notch toughness was previously found. The impact energy values of these specimens correspond more closely to the original air tested values, implying that the loss in impact energy was recovered (Table 2). This indicates the reversible nature of the toughness reduction, linked to the (temporary) presence of hydrogen and not the presence of HICs. A similar conclusion was reached by Wang et al. (2015), who noted a reduction of Charpy absorbed energy when testing immediately after hydrogen charging and found that for specimens placed in air for one day and then tested, the absorbed energy was mostly recovered compared to the as-received specimen.

Table 2. Charpy impact energy values at room temperature for uncharged specimens and specimens charged with hydrogen and then left in vacuum for one week

Charging condition	Charpy impact energy at 20°C (J)
Uncharged	168 ± 18
8h + 1 week H desorption	154 ± 4
48h + 1 week H desorption	158 ± 16

4. Conclusions

The impact toughness of an API 5L X70 pipeline steel was investigated by Charpy impact testing in air and in a hydrogen-charged state. For the tested temperatures (ranging between -80 °C and +20°C), the DBTT was not reached and the material exhibited a rising upper shelf phenomenon. An increase in separation index could be observed on hydrogen-charged samples versus non-charged samples. For lower test temperatures, the effect of hydrogen on the impact toughness disappeared, and no significant difference was observed between uncharged and charged samples for temperatures of -20°C and lower. There was no significant difference in impact energy between samples hydrogen-charged for 8h and for 48h. The presence of hydrogen-induced cracks in the 48h charged samples did not appear to influence the results of the Charpy test. Hydrogen charged specimens generally had more separations at these temperatures. This indicates that hydrogen could promote separations in the specimens, possibly by weakening interfaces vulnerable to delamination and decreasing the through-thickness stress required to trigger a separation. As the decrease in impact toughness seemed to be at least partially related to the occurrence of delaminations for the tested material, the Charpy impact test appears to reflect a H-related weakening of the banded microstructure rather than a pure hydrogen-assisted toughness reduction and is thus highly dependent on specific microstructural factors. This nuanced interpretation should be taken into account when (considering to) adopting Charpy V-notch toughness as a measure of hydrogen embrittlement.

Acknowledgements

The authors acknowledge the support from Research Foundation - Flanders (FWO) via grant G056519N and grant 12ZO420N and the Special Research Fund (BOF) of UGent (grants BOF15/BAS/062, BOF20/BAS/121 and BOF19/GOA/026).

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