Please fill in the name of the event you are preparing this manuscript for.	2022 Abu Dhabi International Petroleum Exhibition & Conference
Please fill in your 6-digit SPE manuscript number.	SPE-211275-MS
Please fill in your manuscript title.	Hydrogen Stress Cracking Resistance Of Seamless Pipes For Hydrogen Storage And Transport Applications

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Abstract

With an increasing number of projects involving production and use of low-carbon hydrogen, the compatibility with hydrogen gas of assets for storage and transport shall be guaranteed. Indeed, hydrogen is a threat for steel equipment integrity as it promotes subcritical crack growth. In this paper the fracture toughness resistance of a selection of seamless pipes and girth weld for pipeline, OCTG and pressure vessel in pure H_2 is investigated. It covers a large variability of materials in terms of microstructures (ferrite-pearlite, bainite, martensite) and yield strengths (from 400 MPa to 700 MPa). Recommendations and requirements provided by ASME B31.12 standard have been followed for this qualification program. Fracture toughness evaluations were performed via fatigue pre-cracked bolt-load specimens exposed to 100 bar hydrogen gas during 1000 h at room temperature. All materials presented hydrogen stress intensity factor thresholds K_{IH} largely above 55 MPa.m$^{1/2}$, compliant with the ASME B31.12 option B requirement that defines materials requirements for hydrogen service. Data provided can be used for building Failure Assessment Diagram, decisive tool for predicting the safe domain of usage of structures.

Introduction

Energy transition is one the main pathway for a decarbonization of the economy. In that view, hydrogen gas is called to play a key role. Initially, assets for energy storage and transport were developed and qualified for the purpose of the oil and gas industry, especially natural gas. Repurposing of existing assets to the use of hydrogen gas is a great challenge for future hydrogen projects. It includes the qualification of steel materials under hydrogen gas environment. There are still a few international standards dedicated to the material selection for hydrogen gas environment. European Industrial Gases Association (EIGA) proposes two documents: IGC Doc 121/14 and IGC Doc 100/03/E for hydrogen pipeline systems and hydrogen cylinders and transport vessels, respectively. For the former, EIGA imposes to limit steel grade to X52 or below, 22 HRC maximum and a hoop stress not more than 30% of Specified Minimum Yield Strength (SMYS). For the latter, materials must be a quenched and tempered 34CrMo4 presenting Ultimate Tensile Strength (UTS) inferior to 950 MPa and a ratio YS/UTS inferior to 0.9. American Society of Mechanical Engineers (ASME) proposes a design code B31.12 for hydrogen piping and pipelines. With option A, steel grades inferior to 65 ksi SMYS can be used with a severe penalty on the maximum acceptable internal pressure. For limiting this penalty option B can be used, which guarantees pipeline integrity in service by the combination of Fracture Toughness (FT) and Fatigue Crack Growth Rate (FCGR) tests for assessing the maximum number of cycles before to reach the maximum acceptable crack length. This paper covers the qualification of a large panel of steel grades for transport and storage of hydrogen gas in accordance with the protocol described into ASME B31.12. Rational behind the employ of this standard will be first discussed.

Rational for material qualification in hydrogen gas

Selection of appropriate test methods starts with the understanding of the micromechanical effect of hydrogen in steels. Even though important research efforts are still produced for that purpose, there is at least consensus on the fact that hydrogen interacts with dislocations:

- Hydrogen forms Cottrell's clouds around dislocations, by segregating on position where the hydrostatic stress is positive[1,2]
- Hydrogen has a screening effect on the repulsive interactions between two dislocations[3,4]. Consequently, separation distance between two dislocations is reduced; in other words the dislocation density increases in presence of hydrogen.
- Hydrogen enhances emission of dislocations and their mobility[5], which corresponds to a reduction of the flow stress
- Hydrogen promotes pile-up of dislocations[6], for instance at grain boundaries.

Such observations fed the building of two major hydrogen embrittlement mechanisms that are Hydrogen Enhanced Localized Plasticity[7] and Adsorption Induced Dislocation Emission[8].

The affinity of hydrogen with tensile hydrostatic stresses is at basis of many simulation works[9] and supports the idea that notch effect is crucial for enhancing hydrogen stress cracking occurrence. Works dealing with Slow Strain Rate Tests (SSRT) of smooth tensile specimens in presence of hydrogen gas did not show hydrogen embrittlement in the uniform deformation domain[10], only beyond UTS when the necking is starting, which actually creates a stress concentration factor. Consequently, methods based on the use of smooth specimens like SSRT[11] or disc test[12] have been discarded for the present material qualification. In addition, such test methods do not provide direct material parameters useable for equipment design. Noticeably disc test standard proposes an acceptance criterion (burst pressure ratio in helium versus hydrogen shall not be above 2) while no consensus exists yet for SSRT, which would require extensive work for fixing some.

With the background that the interaction of hydrogen with dislocations is key in the fracture process of steels in presence of hydrogen, it can be emphasized that hydrogen stress cracking propagation is more likely when the plastic zone ahead of a crack tip has been affected by hydrogen, which means a low straining rate in presence of hydrogen. A too large straining rate and hydrogen has not enough time to diffuse towards the crack and to interact with dislocations. This is the reason why works targeting to find a reduction of Charpy toughness energy failed or lead to very scattered results[13]. A straining before the exposure to hydrogen induces a modification of the dislocation pattern, i.e. a lower dislocation density and a larger plasticized zone contribute to relax more hydrostatic stresses at the crack tip. This is the reason why crack initiation threshold is lower when straining has been done during hydrogen exposure instead of before[14].

ASME B31.12 relies on ASME BPVC.VIII.3 part KD-10 for FT and FCGR test protocols. FT tests can be done either with constant load or constant displacement, implicitly straining in presence or in absence of hydrogen respectively. Indeed, constant load method requires the employ of a tensile frame combined to an autoclave while constant displacement method uses self-loaded specimens. Behind this implicit rule hides the division by 2 imposed by KD-10 document on the applied stress intensity factor $K_{Iapplied}$ to get the hydrogen stress intensity factor threshold K_{IH} when no hydrogen assisted cracking initiates during a constant displacement test. Indeed, factor 2 is approximately what has been found in literature as a derating between crack arrest and pre-strained crack initiation K_{IH}[14].

Interestingly, the same work also observed higher K_{IH} for crack arrest test method compared to crack initiation test method. However, once the crack exceeds the plastic zone formed in air prior the exposure to hydrogen gas, it would have been expected to reach an equivalence between the two values. Authors attributed the gap to the difference of size of plastic zones ahead of the crack when the crack is static or propagating. Another interpretation is to consider the J-R curve used for the calculation of initiation K_{IH} at 0.2 mm offset (Figure 1). On this figure has been added an arbitrary line representing the variation of J with the crack length for a hypothetical crack arrest test. There is a priori no reason for the crack to stop exactly at the position of 0.2 mm offset, which is a convention. Even if less conservative, crack arrest tests are as meaningful as crack initiation tests and constant displacement tests according to ASME B31.12 bring consistent fracture toughness values of steels exposed to hydrogen gas. However, in the case of a lack of cracking after constant displacement test, the issue is that the division by 2 is very likely overly conservative because there is no clue that the selected $K_{Iapplied}$ was close to the threshold value to start crack propagation.

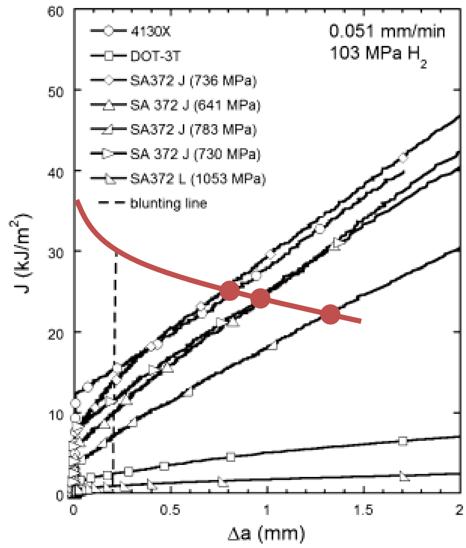

Figure 1: J-R curve taken from ref. 14; red line and dots have been added on the original figure and arbitrary represent the situation of a crack arrest test for which the initial J value has been imposed in air and decreases with the crack length. Initiation K_{IH} was calculated by Nibur and al. from J 0.2mm offset (vertical interrupted line).

Experimental

Materials and environment

Seamless pipe grades were produced by Vallourec and selected for covering a wide range of applications, microstructures and yield strengths (Table 1). X65 linepipe grade is a bainitic material where test specimens were sampled in base metal (BM), Heat-Affected Zone (HAZ) and Weld Metal (WM). Weld was produced by Serimax in 1G condition. Selected OCTG grades were ferritic-pearlitic materials in grade 55 ksi, adapted for either welded joint or connection joint, and quenched and tempered API 5CT L80 presenting a martensitic microstructure. The last material is also a martensitic grade used for pressure vessels with the composition 34CrMo4.

Table 1: List of materials selected for the test program.

Material	Application	Microstructure	OD x WT	Sampling	YS /MPa (ksi)
X65 +girth weld	Linepipe	Bainitic (Parent metal)	321.6 x 15.90	Base metal Heat-affect. zone Weld metal	524 (76.0) (Base metal)
Weldable 55 ksi	OCTG (welded joint)	Ferritic-pearlitic	273.1 x 13.84	Base metal	466 (67.6)
K55	OCTG (connection joint)	Ferritic-pearlitic	339.7 x 12.19	Base metal	415 (60.2)
L80 type 1	OCTG (connection joint)	Martensitic	159 x 21.2	Base metal	589 (85.4)
34CrMo4	Pressure vessel	Martensitic	492.40 x 65.10	Base metal	708 (102.7)

Fracture toughness tests

Fracture toughness tests were performed in two laboratories (A & B) according to ASTM E1681. Bolt-load compact specimens were sampled in orientation T-L (Transverse-Longitudinal) for base metal and N-P (Normal-Parallel) for heat-affected zone or weld metal (Figure 2).

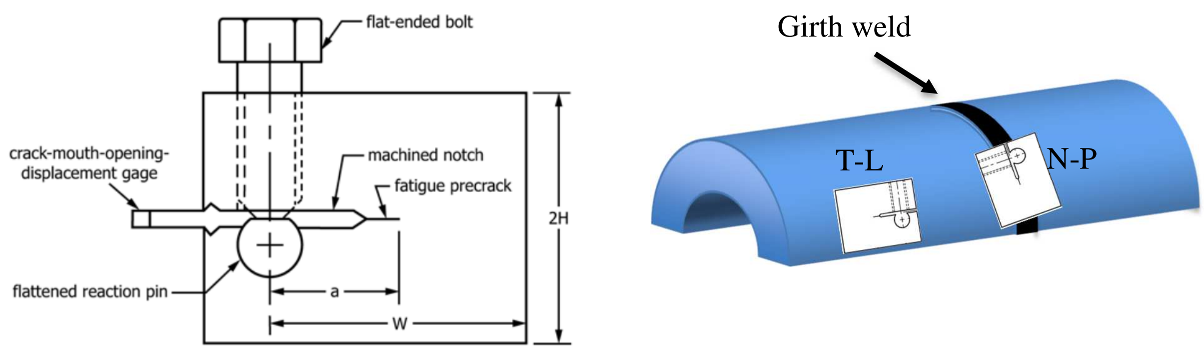

Figure 2: (Left) Modified bolt-load compact specimen according to ASTM E1681; (Right) Specimen orientation on parent pipe or girth weld.

Three to five specimens were tested per material. Specimen thicknesses were at least 85% of the pipe thickness except for the very thick pressure vessel pipe, for which the thickness was limited to 34 mm in lab A and 18 mm in lab B. Specimens were fatigue pre-cracked prior the mechanical loading. Loads were selected for imposing an initial stress intensity factor as high as possible and based on recommendations provided by ASME BPVC.VIII.3 part KD-10 for ferritic steels. After introduction inside the autoclave, specimens were exposed during at least 1 000 h to 100 bar high purity hydrogen gas at room temperature (95 bar H_2 for lab B due to autoclave limitation). After exposure, specimens were opened and the fracture surfaces carefully examined. If the specimen showed hydrogen assisted subcritical crack growth at least 0.25 mm long beyond the fatigue pre-crack, hydrogen stress intensity factor threshold K_{IH} is directly calculated from ASTM E1681 formula for bolt-load compact specimen using initially applied Crack-Mouth Opening Displacement (CMOD) and final crack length. Otherwise, K_{IH} is considered at least equal to the half value of $K_{Iapplied}$ according to KD-10 document and as reminded in the introduction.

Results and discussion

Table 2 summarizes results of fracture toughness tests. Only one set of specimens showed sufficient subcritical crack growth: K55 tested in lab A as illustrated in Figure 3. For this material, average K_{IH} value is equal to 113.6 MPa.m$^{1/2}$. For all others material sets, K_{IH} are considered superior to $K_{Iapplied}$ divided by 2. X65 including the weld itself present K_{IH} above 67 MPa.m$^{1/2}$, weldable 55 ksi above 87.5 MPa.m$^{1/}$, L80 above 78.0 MPa.m$^{1/2}$ and 34CrMo4 above 70.2 MPa.m$^{1/2}$. From these results, it can be concluded that all materials are suitable for service under 100 bar H_2 gas based on ASME B31.12 requirements of 55 MPa.m$^{1/2}$ minimum for the hydrogen stress intensity factor threshold. Such fracture toughness values should be sufficiently high for insuring safe equipment design based on engineering critical assessment approach. Moreover, it can be argued that these materials are also suitable for higher pressures of hydrogen considering the quite limited impact of this environmental parameter beyond approximately 50 bar based on the large literature review performed by SANDIA[15]; e.g. X60 and X80 materials presented the same K_{IH} at 55 and 210 bar of dihydrogen.

For cracked K55 material set, the higher $K_{Iapplied}$, the higher K_{IH} is. Such observation has already been discussed by Somerday et al.[16] who attributed this phenomenon to a difference on crack-tip strain fields between a stationary and a propagating crack. The reason why K55 presented a subcritical crack growth and not the other materials is not clear. It could be attributed to a higher intrinsic susceptibility to hydrogen of ferritic microstructures compared to tempered bainite or martensite but this ranking is normally valuable only for equivalent mechanical properties[17] and K55 was the pipe presenting the lowest yield strength. Moreover, the same grade did not crack in lab B. Noticeably, K55 has been the single grade tested in a separated test batch in lab A; this may highlight a sensitivity of this test method to testing conditions.

Conservatism due to the division by two of $K_{Iapplied}$ in the absence of cracking is clearly evidenced. Indeed, while K_{IH} of K55 is approximately 114 MPa.m$^{1/2}$ in lab A where specimens cracked, it becomes 87 MPa.m$^{1/2}$ minimum in lab B.

All K_{IH} values in Table 2, minimum expected values or calculated values, do not respect the primary plane strain validity criteria of ASTM E1681. Consequently, bolt-load compact specimens should have overpassed their linear elastic regime. This observation argues for the use of alternative fracture toughness methods able to include non linear contributions like those described in ASTM E1820.

Table 2: Fracture toughness values of a selection of steel grades under 100 bar of H_2.

Material	Notch Position	Orientation	Lab	Number of specimens	$K_{Iapplied}$ /MPa.m$^{1/2}$	Crack growth*	K_{IH} /MPa.m$^{1/2}$
X65 +girth weld	BM	T-L	A	4	141-145	No	>70.5
			B	3	105-106	No	>52.5
	HAZ	N-P	A	4	135-142	No	>67.5
			B	3	104-106	No	>52.0
	WM	N-P	A	4	134-147	No	>67.0
			B	3	104-105	No	>52.0
Weldable 55 ksi	BM	T-L	A	4	138-143	No	>69.0
			B	3	175-176	No	>87.5
K55	BM	T-L	A	4	129 132 136 159	Yes	106.3 105.8 116.5 125.6
			B	3	174-176	No	>87.0
L80 type 1	BM	T-L	A	5	140-165	No	>70.0
			B	3	156-157	No	>78.0
34CrMo4	BM	T-L	A	4	140.4-143.0	No	>70.2
			B	3	117-118	No	>58.5

*Yes when hydrogen assisted cracking exceeds 0.25 mm according to ASME BPVC.VIII.3 part KD-10.

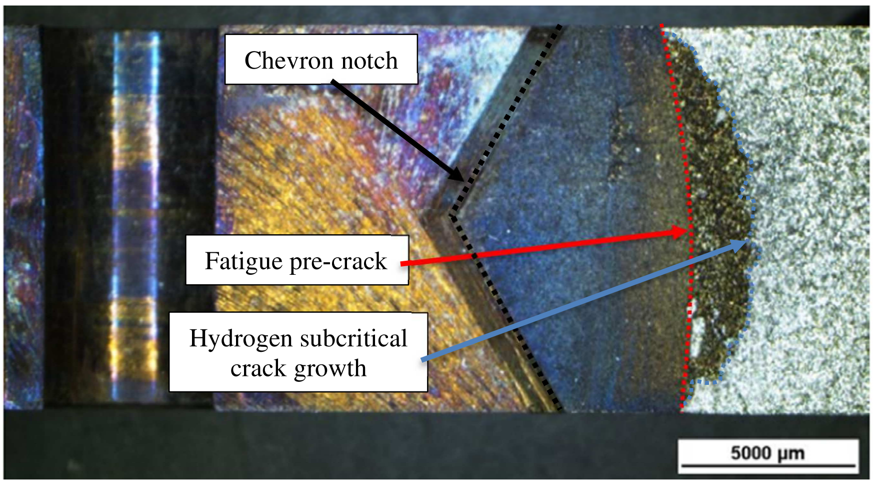

Figure 3: Observation of hydrogen assisted subcritical crack growth in K55 after exposure to 100 bar of H_2.

Conclusions and perspectives

Fracture toughness tests according to ASTM E1681 based on impositions of ASME B31.12 have been performed on a selection of seamless steel pipes to be used for hydrogen transport and storage applications. Bolt-load compact specimens were sampled to T-L direction for base metal and N-P direction for weldment and exposed to 100 bar H_2 during 1000 h. All materials display hydrogen stress intensity factor thresholds K_{IH} well above code limit of 55 MPa.m$^{1/2}$, compliant with the ASME B31.12 option B requirement that defines materials requirements for hydrogen service. This confirms the suitability of Vallourec's pipes for hydrogen service in different applications.

It has been observed that the crack arrest test method is very conservative. In absence of hydrogen cracking during the exposure, it was expected a severe reduction on the estimated value of K_{IH}. This has been confirmed experimentally on K55.

A test program is in progress with additional test batches of higher strength materials such as X80 linepipe, or 95 and 110 ksi OCTG grades. Fatigue crack growth rates in the same environment are also in progress at 1 Hz or 0.1 Hz and for load ratios at 0.1 or 0.9 for covering applications with cycling loading representative for very different internal pressure variations during service life.

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