EFFECTS OF PURITY AND PRESSURE ON THE HYDROGEN EMBRITTLEMENT OF STEELS AND OTHER METALLIC MATERIALS

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ABSTRACT

A study of open literature was performed to determine the effects of high hydrogen purity and gas pressure (in the range of 700-1000 bar) on the hydrogen embrittlement of several metallic materials. A particular focus was given to carbon, low-alloy, and stainless steels, but information on embrittlement of aluminum and copper was included in the study. Additionally, the most common test methods were studied, and results from similar tests are presented in a manner so as to simplify comparisons of materials. Finally, suggestions are provided for future testing necessary to ensure the safety of hydrogen storage at 700 bar.

1.0 INTRODUCTION

Hydrogen embrittlement is a well-known phenomenon of the degradation of mechanical properties of steels in the presence of hydrogen. An important result of embrittlement (hereafter referred to as HE) is premature failure for structural metals in pipeline steels and hydrogen transport cylinders. In the near future, as economies begin to utilize hydrogen as an energy source, specific applications such as fuel cells will require storage at very high hydrogen pressures in order to provide competitive ranges with current gas-powered vehicles. Because of the volatility of the gas, failure of storage vessels poses a significant risk, and a feasible solution must be developed in order to ensure the safety of the public.

The embrittlement of steels depends on a variety of factors such as the environment, material, and surface state of the metal. The environment includes the hydrogen gas pressure, purity, temperature, exposure time, stress, and strain rate. Material properties of the steel include microstructure, chemical composition, mechanical properties, cold working, welding, and heat treatment [3]. Finally, the surface state of the metal refers to stress concentrations, defects such as cracks and notches, and prior surface treatments of the metal [1].

A multitude of studies have examined the effects of hydrogen embrittlement on various metals. For steels in particular, austenitic stainless steels consistently demonstrate the best performance in hydrogen environments and do not suffer from the high level of susceptibility of ferritics to HE. Steels with martensitic structures are extremely sensitive to the effects of embrittlement and are poor choices for use in hydrogen environments [4].

Embrittlement of steels can occur from either internal or external hydrogen exposure. Internal HE results from the presence of excess hydrogen introduced during manufacturing processes and is governed by the diffusion of the gas into the metal. Simulation of this process is performed by internal hydrogen charging tests. External HE is caused by the presence of gaseous hydrogen and, for most materials, has a maximum effect at room temperature (about 20ºC). In external HE, the hydrogen diffuses in a metal through dislocations during loading, and testing methods require the use of hydrogen gas to properly simulate service conditions [2].

A literature survey has been conducted with a focus on external hydrogen embrittlement in low alloy, carbon, and stainless steels in high purity hydrogen as well as H_2 pressures from 700-1000 bar. Results presented are from tests performed in gaseous hydrogen environments unless otherwise stated. The study also includes an examination of the most effective testing methods to simulate the operating conditions and understand HE in high pressure hydrogen storage vessels. The survey included the study of approximately 50 documents, of which 22 were relevant to the aforementioned topics. Of these, 11 provided detailed information on the types of testing methods, 12 discussed the effects of gas purity on HE, and 17 contained information about hydrogen at high pressure. The goal of the study was to collect summarize current knowledge in order to develop an understanding of HE for high pressure storage in the future of hydrogen energy applications.

2.0 TESTING METHODS

In order for a test to provide worthwhile information on the susceptibility of a metal to HE, it must accurately simulate operating conditions and have clearly defined variables. For the study of hydrogen embrittlement, many possible variables exist even for a single testing method, and as a result, data can often be difficult to compare. However, from the gathered literature, it is clear that several testing methods have gained prevalence over the past 4 decades because of the relevance of the performance characteristics they provide for steels in hydrogen environments.

2.1 Tensile Tests

Tensile testing requires straining a specimen until rupture in order to determine the effects of hydrogen on ductility, or deformation capacity, and strength of the material. Reduction of area,

$$\%RA = \frac{A_i - A_f}{A_i} x100\%$$

is often used as a measure of ductility, where A_i and A_f are the initial and final cross-sectional areas, respectively, for the specimen. Additionally, % elongation of the specimen during testing is used to describe the level of ductility. The reduction of area loss, %RAL, is used to compare the %RA of a specimen for tensile tests in hydrogen as opposed to a more inert gas, such as helium, air, or nitrogen. Tensile testing is also used to determine the effects of H_2 on yield and ultimate tensile strength (UTS), and it can be performed on samples that have been cathodically charged, exposed to gaseous hydrogen, or both. Specimens can be either smooth or notched, the latter simulating the scenario of an operational metal with surface flaws. Variables for tensile tests, other than pre-treatments of the material, include gas pressure, gas purity, temperature, and strain rate. An alternative form of tensile testing is a delayed rupture test in which a specimen is loaded to a constant value in a hydrogen environment until rupture occurs.

While tensile tests are capable of showing the effects of hydrogen on ductility and strength, the method is limited in that all stresses are uniaxial and it does not simulate the multiple stresses present in pressure vessels [5].

2.2 Fracture Mechanics Tests

Fracture mechanics testing creates a planar stress state (an advantage over the uniaxial stress in tensile tests) to analyze crack growth for precracked specimens in hydrogen environments. Environmental factors such as gas purity, pressure, and temperature can be varied and comparisons made with properties under similar loadings in helium, nitrogen, or air. The two primary types of fracture mechanics methods are Wedge Opening Load (WOL) and Compact Tension (CT) tests [1].

2.3 Wedge Opening Load (WOL)

This type of test is used to determine the static load threshold stress intensity factor (K_{TH} or K_H), which is the stress intensity factor at crack arrest. WOL tests are also used to measure crack growth rates (da/dt) or simply crack growth. High threshold stress intensity factors and low crack growth rates in hydrogen environments signal high resistance to HE for a metal specimen. The ISO 11114-4 [20] standard states that an acceptance criteria for maximum crack growth is 0.25 mm.

2.4 Compact Tension (CT)

Compact tension tests are conducted to determine the effect of hydrogen on fatigue crack growth rate (da/dN) in a range of pressures and frequencies to compare with reference data from an inert environment. CT tests can also be used to find threshold stress intensity factor, K_{TH}, and plane-strain fracture toughness, K_{IC}.

Key variables in CT fatigue tests (other than environmental factors) are the stress intensity factor range ($\Delta K = K_{max} - K_{min}$), loading frequency, crack length, and number of cycles [17]. For threshold stress intensity factor, ISO 11114-4 provides an acceptance criteria that the value of K_{TH} be greater than (60/950) x R_m (MPa-m$^{0.5}$), where R_m is the ultimate tensile strength of the material [20].

2.5 Disk Testing Methods

Disk tests are used to determine the effect of hydrogen gas on steel rupture by using helium as a reference gas. Specimens of 58mm diameter and 0.75mm thickness are clamped between two steel flasks and pressurized until rupture. Several types of disk tests exist, and an advantage of utilizing disk testing over other methods is that a triaxial stress state is created which more closely replicates the stresses of a pressurized storage vessel [1].

2.6 Disk Rupture test

This form of test uses gas pressurization from a single side of the disk until rupture occurs, with helium being used as a reference gas for comparison with hydrogen. The pressure increase rate is an important control in the test, and the respective rupture pressures, PHe and PH_2, are used to find an embrittling index, PHe/ PH_2. Results from a rupture test are shown in Figure 1, as reproduced from H. Barthélémy [2], showing the effects of pressure increase rate on the HE index.

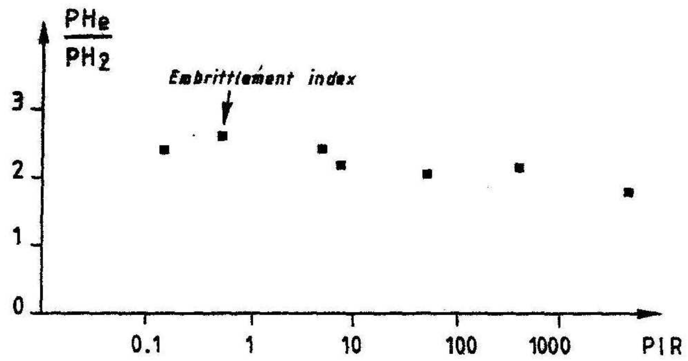


Figure 1. Effect of Pressure Increase Rate (PIR, in bar/min.) on the embrittlement index of an unspecified steel during disk rupture testing [2]

H. Barthélémy and G.M. Pressouyre (1985) [1] state that an index of 2.0 should be used as a threshold of acceptability, as steels with an equal or lower index have shown safe behaviour in the past in hydrogen environments. A disadvantage of this test, however, is that the embrittlement index is only a relative measurement. As a result, this test is valuable for evaluating the relative susceptibility of a specific metal, but it is limited to only providing the final burst pressure when attempting to quantify safety of a component during operation [10].

2.7 Disk Delayed Rupture test

This test is very similar to the rupture test, but the disk is instead loaded to a constant value below the rupture pressure. Embrittlement is demonstrated by premature rupture in the presence of hydrogen.

2.8 Disk Fatigue test

Several variants of disk fatigue tests exist. The first method is to expose both sides of the disk to pressurized hydrogen. One side is maintained at a constant pressure, while the other has a very small volume to allow cyclic pressure changes through the use of a hydraulic system. This method is used to count the number of cycles to rupture, with the possibility of varying frequency and the amplitude of the pressure, ΔP. The second method includes the same variables but instead alternately pressurizes each side of the disk to the maximum pressure. Finally, the third method, as discussed by H. Barthélémy and G.M. Pressouyre [1], resembles the first method in that pressurization occurs from only one side. However, a displacement gauge on the upper portion of the disk detects deflection, thus providing the pressure at which maximum deflection and thus maximum crack propagation occur. The advantage of this and the other disk fatigue tests is the realistic modelling of a pressure vessel undergoing filling and emptying, with a numerical result for the number of cycles before failure occurs.

3.0 THE EFFECTS OF HIGH PRESSURE ON HE

Hydrogen embrittlement of steels and other materials has been well-documented for extensive pressure ranges. The study focused primarily on pressures from 700-1000 bar, but other data was also relevant to the study in order to understand the embrittlement trends for increasing pressure. An objective was to determine if the effects of embrittlement were maximized at a pressure lower than rupture, with properties becoming pressure-independent at higher levels. This section is a summary of results from the available literature for pressure effects on HE.

3.1 Disk and Tensile Test Results

H. Barthélémy [2] presented data from disk rupture tests on AISI 321 steel. In these tests, the effect of hydrogen partial pressure was studied by increasing the H_2 pressure to a specific level before adding helium until rupture. The hydrogen partial pressure at which maximum embrittlement occurred was reported to be between 20 and 100 bar. Figure 2 from Reference 2 shows the results of the test, with embrittlement increasing very quickly at low pressures before reaching a constant level near 25 bar.

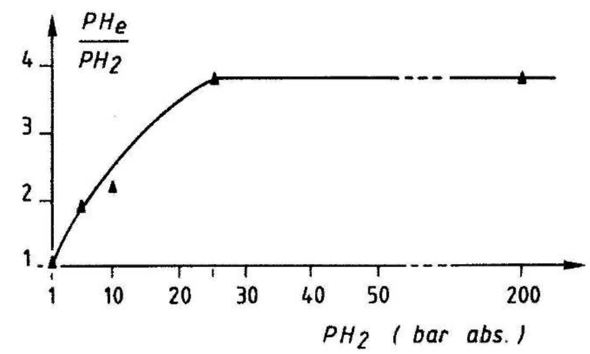


Figure 2. Effect of hydrogen partial pressure on the embrittlement index of AISI 321 steel [2]

In tests performed by Elices and Gutierrez-Solana (1982) [6] on a typical Spanish pipeline carbon steel similar to X-42, tensile tests on double-notched specimens showed significant reduction in area losses at hydrogen pressures near 7 MPa. As shown in Figure 3, the trend continues upward in a steady, but much more stable, slope until the upper limit of the testing procedures at 35 MPa. Although the data appears to show a continual increase, it is possible that the %RAL reaches a threshold at higher pressure. This may be a property of the X-42 type steel exhibiting different behaviour from the AISI 321 shown in Figure 2.

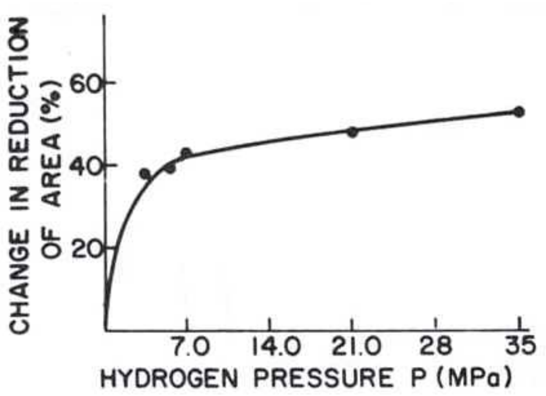


Figure 3. Influence of hydrogen pressure on reduction in area losses for steel similar to X-42 [6]

From the tests of M. Elices and F. Gutierrez-Solana, it was reported that strength-related properties were unaffected by the presence of hydrogen. Similarly, in much of the literature studied, the presence of hydrogen did not significantly affect the strength of smooth tensile specimens. For notched samples, however, high pressure hydrogen often caused losses in strength as well as more significant losses in ductility. K. Xu (2005) [8] presented results from previous data for carbon steels in which tensile tests were performed in hydrogen from 1000 to 10,000 psig (6.89-689 bar). The data is provided in Table 1, illustrating substantial ductility losses for both types of specimens in high and low pressure hydrogen, as well as moderate strength losses for the notched samples. Because the results came from different types of steels, it is not exactly clear how behaviour was affected over the pressure range. The steels tested at 1000 psig experienced greater differences in %RAL between smooth and notched specimens, but it appears that the higher pressure caused more degradation in the strength of the notched specimens.

Table 1. Tensile properties of carbon steels in hydrogen environments [8]

	TS (ksi)			% RA		
	10000 psig He	10000 psig H2	% change	10000 psig He	10000 psig H2	% change
1042 normalized smooth	90	89	0	59	27	-54
1042 normalized notched	153	115	-25	8.5	2.8	-67
	Air	1000 psig H2	% change	Air	1000 psig H2	% change
A516 smooth	78	80	3	70	43	-39
A516 notched	110	91	-17	30	5	-74
SA106-B smooth	81	84	4	58	50	-14
SA106-B notched	106	98	-9	26	8	-69
X42 smooth	74	70	-5	56	44	-21

Not all steels, however, were affected in the same way by tensile tests in hydrogen gas. C. San Marchi and B. Somerday (2007) [10] of Sandia National Laboratories compiled a sizeable report on the effects of hydrogen for numerous metals, and the results vary considerably depending on the metal composition.

As carbon steels have demonstrated significant ductility losses in hydrogen, the same is true for low and high-alloy ferritic steels exposed to gas at 69 MPa pressure. Martensitic steels, like 9Ni-4Co, showed extreme susceptibility to embrittlement. In general, the effects of embrittlement are worse for materials with higher yield strengths.

High alloy austenitic steels showed varying results in hydrogen testing. Type 304 steels showed medium to high ductility losses (from about 10% to almost 50%, depending on heat treatment) for smooth specimens. Type 316 stainless steels experienced low ductility losses when thermally precharged with hydrogen, but almost no ductility losses occurred in room temperature gaseous hydrogen at 69 MPa, either for smooth or notched samples. See Table 2 [10].

Although high nitrogen content generally lowers resistance to embrittlement, it was found that several stainless steels with <0.3 wt% nitrogen performed well in external hydrogen. Nitrogen-strengthened 22Cr-13Ni- 5Mn stainless steels showed little HE effect at 69 MPa, but large ductility losses were recorded for precharged specimens tested at 172 MPa. It appears the precharging increased susceptibility to HE more than the increased pressure, as uncharged nitrogen-strengthened 21Cr-6Ni-9Mn experienced only slight ductility losses in 172 MPa external hydrogen gas.

Table 2. Tensile properties of 316 stainless steel in high pressure hydrogen gas [10]

Material	Thermal precharging	Test environment	Strain rate (s^{-1})	S_y (MPa)	S_u (MPa)	El_u (%)	El_t (%)	RA (%)
Not specified	None	69 MPa He	---	214	496	---	68	78
	None	69 MPa H_2		214	524	---	72	77
Cold drawn rod, heat W69	None	69 MPa He	0.67 x10^{-3}	441	648	---	59	72
	None	69 MPa H_2		---	683	---	56	75
Annealed plate, heat O76	None	Air	3 x10^{-3}	262	579	---	68	78
	None	69 MPa H_2		221	524	---	72	77
Annealed sheet	None	Air	0.6 x10^{-3}	263	568	---	90	75
	None	70 MPa He		248	565	---	85	70
	None	70 MPa H_2		249	566	---	85	75

3.2 Fracture Mechanics Test Results

The effects of hydrogen pressure have also been extensively reported for fracture mechanics tests. The most common results of increased hydrogen pressure are decreased cracking threshold values and fracture toughness. Similar to tensile tests, however, the results vary depending on the type of steel.

3.3 Threshold Stress Intensity Factor, K_{TH}

K. Xu [8] presented data for threshold stress intensity factors from WOL tests for several types of steels, which were categorized as resistant, moderately susceptible, and highly susceptible to HE. Type

304 stainless steel as well as A516, A106, and HY-80 carbon steels resisted crack propagation at 69 and 97 MPa. Moderately affected steel, 4130, had K_{TH} values of 68, 45, and 32 MPa√m at hydrogen pressures of 41, 62, and 69 MPa, respectively. Thus, the apparent trend was a decrease of threshold stress intensity with increasing H_2 pressure. A discrepancy occurred within the data, however, because the stress intensity factor at 97 MPa was measured to be 52 MPa√m, which was greater than the values measured at 62 and 69 MPa. Similar discrepancies occurred for other steels categorized to be moderately susceptible to embrittlement, as can be seen in Figure 4. Highly susceptible steels, however, consistently had lower K_{TH} values at higher hydrogen pressures.

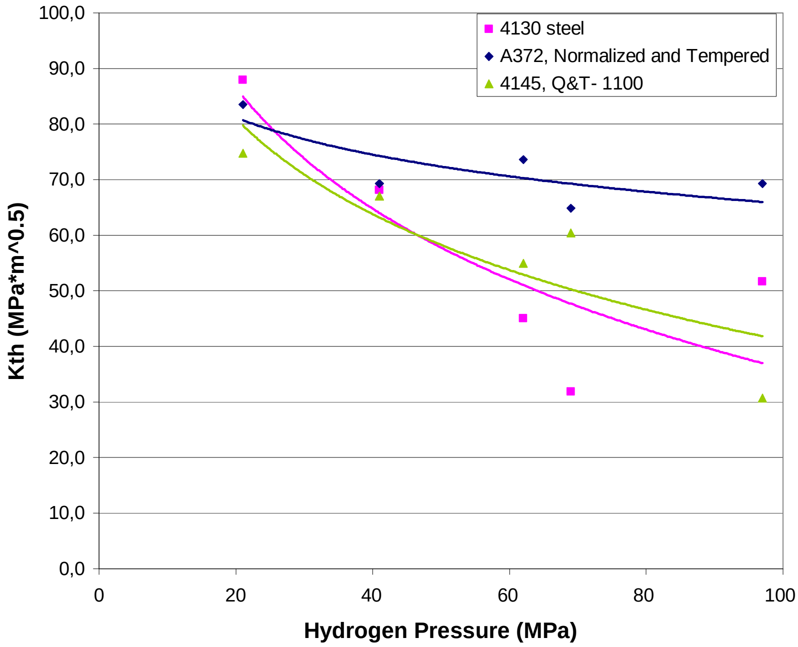


Figure 4. Threshold stress intensity factors for several moderately affected carbon steels [8]

T.M. Adams, P.S. Lam, and R.L. Sindelar (2007) [17] presented information from the same set of data as K. Xu in which the results for K_{TH} were averaged based on yield strength values of the steels. The result revealed two distinct trends, one for steels with yield strengths from 586 to 779 MPa and another for yield strengths from 869 to 1055 MPa, which illustrated decreasing average stress intensity factor as hydrogen pressure increased from 21 to 97 MPa. The trends, in which lower strength steels demonstrated higher resistance to HE, are shown in Figure 5. The data for higher yield strength steels appears to reach a limiting value for pressures above 60 MPa, whereas the lower strength steels do not approach a limit below a pressure of 100 MPa.

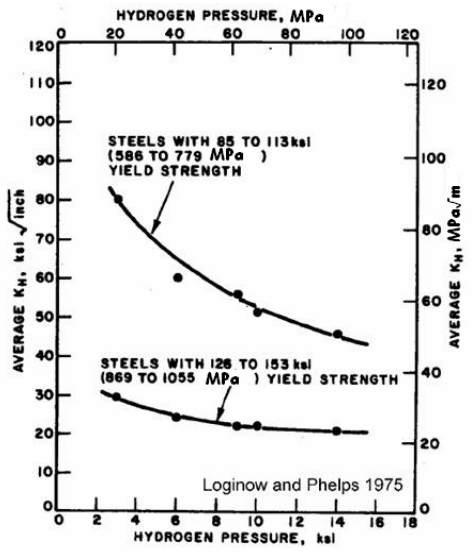


Figure 5: Influence of hydrogen pressure on threshold stress intensity factor at crack arrest [17]

Additional test data from C. San Marchi and B. Somerday [9, 10] illustrated a similar inverse relationship between cracking threshold and hydrogen pressure. Figure 6 shows the trend for low-alloy Cr-Mo ferritic steels, which appear to approach a limiting KTH value. Additionally, the much higher cracking threshold of A-286 stainless steel is included at 200 MPa. A-286 was reported to have no significant change in KTH from 100 to 200 MPa hydrogen, and a high energy rate forged (HERF) 316 stainless steel resisted crack propagation at these pressures. These steels appear to be exceptions, however. Figure 7 shows data for two ferritic steels, which follow similar trends to previous examples, including the steel of lower strength having higher resistance to HE. Although the data for 4130 appears inconsistent past 60 MPa, type 4147 appears to reach a threshold KTH value of 20 MPa√m at 60 MPa, beyond which pressure does not significantly affect KTH.

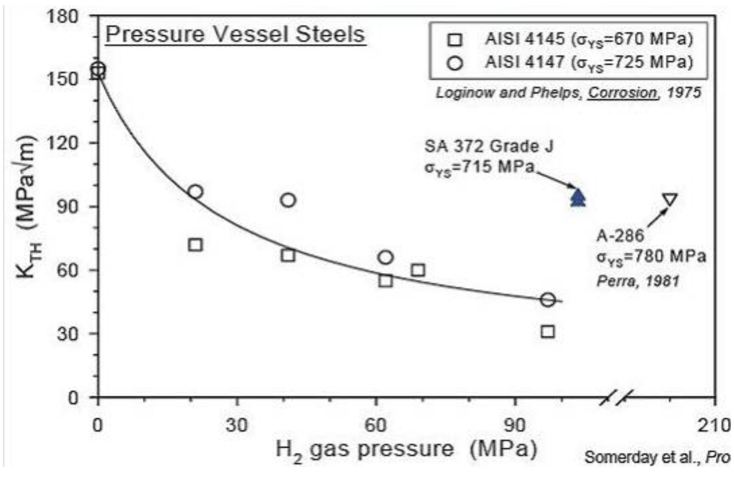


Figure 6. Influence of hydrogen pressure on KTH for several steels [9]

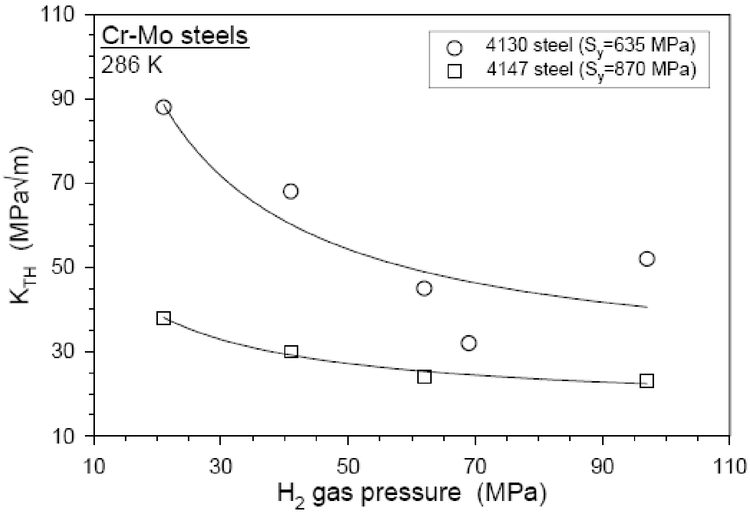


Figure 7. KTH for two ferritic steels. HE appears to have little effect on type 4147 at pressures higher than 60 MPa [10]

3.4 Fracture Toughness

Fracture toughness tests have revealed similar trends to stress intensity cracking threshold values. The presence of hydrogen gas causes significant decreases in toughness, and increased pressure leads to further decrease. Tests have been performed on an extensive variety of steels, providing data for plane-strain fracture toughness, K_{IC}, and elastic-plastic fracture toughness, J_{IC}. Fracture toughness data from several sources consistently showed severe effects due to hydrogen at low pressures before reaching a limiting value, after which increased pressure had little effect. For example, fracture toughness for carbon steels declined as much as 50% in hydrogen at 6.9 MPa, but values appeared to reach a limiting value in the range of 20 MPa [10]. The toughness was also reported to depend strongly on loading rates, with higher K_{IC} values obtained at higher loading rates. Results of fracture toughness tests up to 34.5 MPa on two carbon steels, X-42 and A-516 Grade 70, are shown in Figure 8.

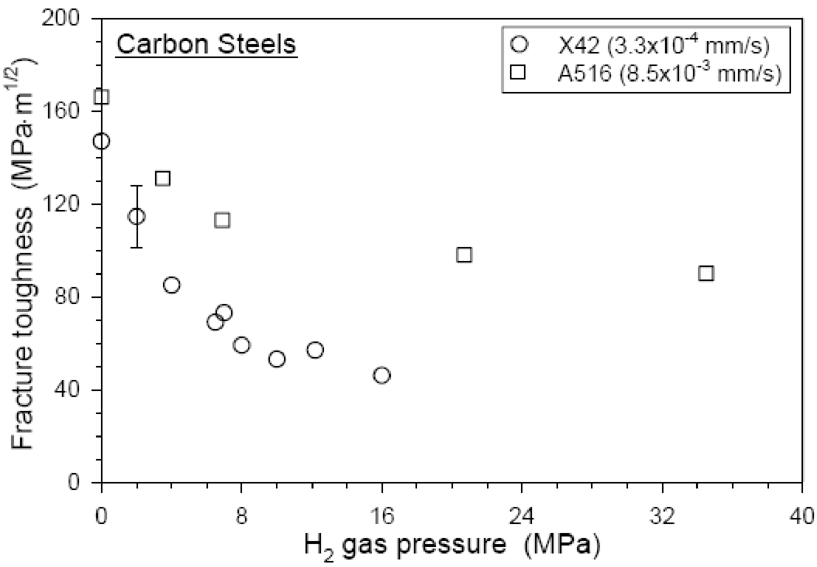


Figure 8: KIC for carbon steels. Fracture toughness decreases significantly at low hydrogen pressure before reaching a limiting value [10]

For a comparison of steels tested for toughness at the same loading rates, micro-alloyed X-42 and X-52 steels were tested against two different forms of SA-106 up to 4000 psi (28 MPa). Figure 9 shows the results, in which the X-42 and X-52 demonstrated much higher elastic-plastic fracture toughness, J_{IC}, at a loading rate of 0.002 in/min (0.0508 mm/min) [8]. All samples appeared to approach a limiting toughness past 2500 psi (17 MPa).

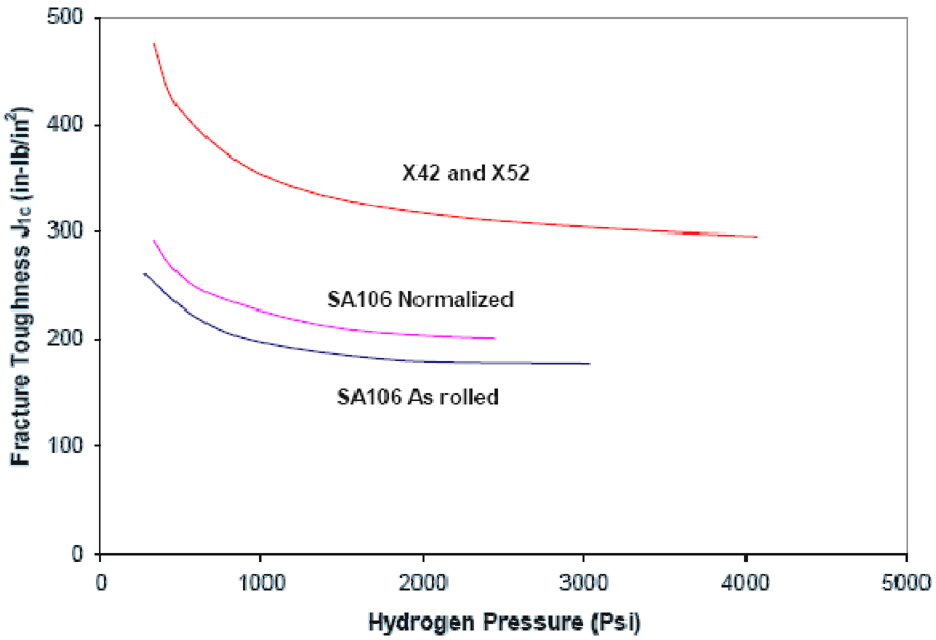


Figure 9. KIC for linepipe steels. Fracture toughness for tests performed at a loading rate of 0.002 in/min [8]

Unfortunately, few sources provided significant fracture toughness data at hydrogen pressures within the 700-1000 bar range. Limited data was reported for 22Cr-13Ni-5Mn nitrogen-strengthened steel, which was tested in helium and hydrogen gases at 69 MPa. Tests of J-integral fracture toughness showed the effects on forged bars of tests run parallel and perpendicular to forge flow lines, with toughness decreasing by 28% in the parallel test and almost 90% in the perpendicular test as compared to properties in helium at the same pressure. However, this was one of few fracture toughness tests performed at high pressures.

3.5 Fatigue Crack Growth (Disk or Fracture Mechanics tests)

The effects of hydrogen gas on fatigue crack growth rate (FCGR) are amongst the most significant data covered by this study, as fatigue crack is of utmost concern when discussing high pressure gas cylinders undergoing frequent emptying and refilling. The fatigue crack growth rate, da/dN, depends strongly on the loading frequency, the stress intensity range (ΔK), and the environmental properties of the gas. Data reported in the literature covered tests performed using a wide range of variables, and a summary of the most relevant information is covered below.

According to Adams et al [17], tests on X-42 carbon steel showed fatigue crack growth rate to be 150 times greater in hydrogen gas than in nitrogen at 6.9 MPa. Similarly, for low alloy ferritic steels, hydrogen significantly increased FCGR compared to specimens tested in helium. For tests on HY-100 steel at 52 MPa with a cycling frequency of 1 Hz, crack growth continued to increase steadily with the value of ΔK up to about 100 MPa√m [10]. Figure 10 is reproduced from Reference 10 to show the trends in both hydrogen and helium gas.

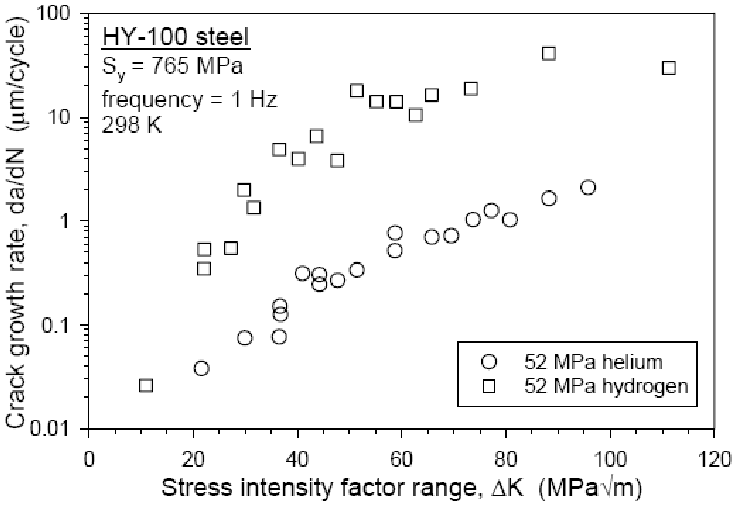


Figure 10. Fatigue crack growth rate vs. stress-intensity factor range for tests of HY-100 steel at 52 MPa [10]

Yield strength appeared to have an opposite effect on fatigue crack than on KTH, with low strength steels experiencing greater acceleration of crack growth in hydrogen than high strength steels. Additionally, tests of ASME SA-105 Grade II steel at 103.4 MPa showed that higher cycling frequencies led to slower crack growth rates [17]. Tests were performed with a stress ratio, R, of 0.1, and the results from Reference 17 are shown in Figure 11. Data from helium tests at 34.5 MPa are also shown, illustrating the significantly lower crack growth rates in an inert gas.

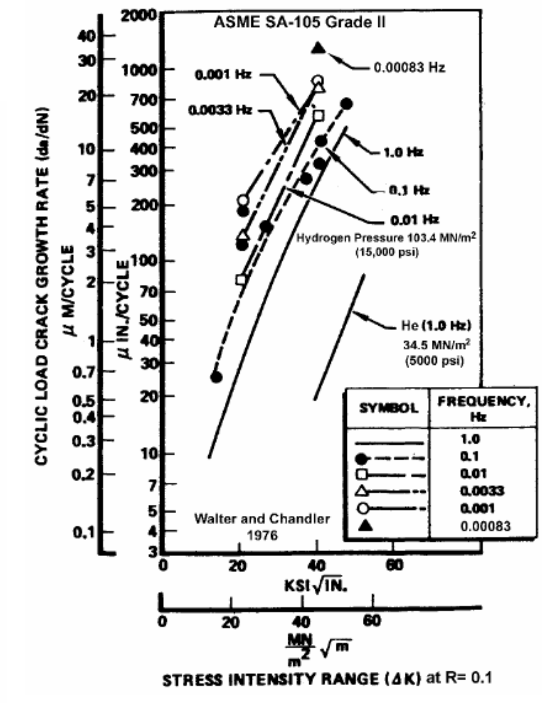


Figure 11. FCGR vs. ΔK for SA-105 steel at 103.4 MPa [17]

Reported effects of pressure on fatigue crack varied throughout the literature. H. Barthélémy and G.M. Pressouyre [1] provided data from tests performed by British Steel on 1% Cr-Mo steel at 1 Hz which demonstrated a clear increase of FCGR in hydrogen from 41 to 152 bar, but no significant difference between 1 bar compared to 41 bar.

C. San Marchi and B. Somerday [10] stated that crack growth rates increased with hydrogen pressure. This was supported by data for HY-100 steel tested at 1 Hz in room temperature with a stress range of 55 MPa√m. As can be seen in Figure 12, the data demonstrated increasing da/dN for hydrogen gas pressures up to 100 MPa.

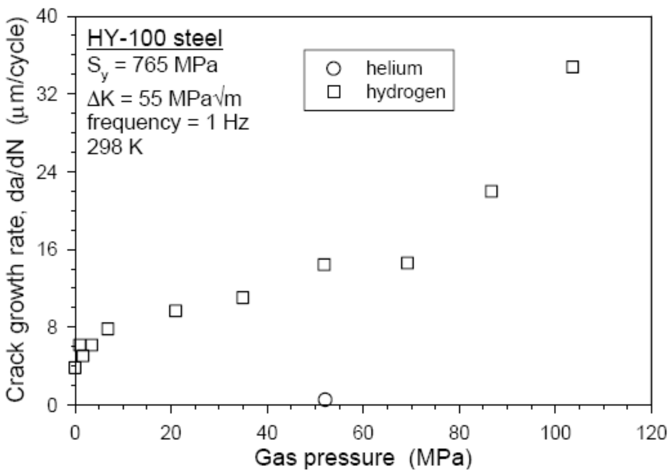


Figure 12. Pressure-dependent FCGR for HY-100 steel [10]

Other sources, however, reported data showing a differing relationship between crack growth rate and hydrogen pressure. Xu [8] reported that hydrogen presence increased fatigue crack growth rate 20 to 50 times compared with air for tests with stress ration R=0.1 at 20.7 MPa. However, FCGR was not sensitive to pressures from about 200-4000 psi (1.4-28 MPa) for stress intensity range ΔK= 20 ksi√in (22 MPa√m), as can be seen from Figure 13 [8].

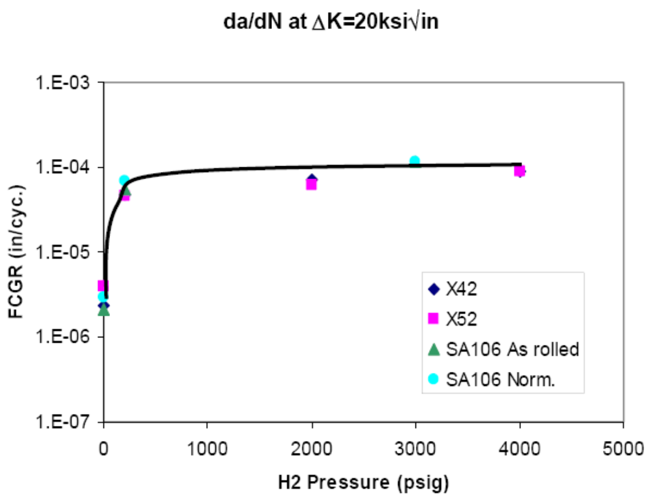


Figure 13: FCGR vs. Pressure for several carbon steels at ΔK= 20 ksi√in [8]

For specimens of SA-105 Grade II steel, for which frequency-dependent results are provided in Figure 11, tests were also conducted at pressures of 6.9, 68.9, and 103.4 MPa over the same stress intensity range. Adams et al reported that, for ΔK>33 MPa√m, the gas pressure did not have any effect on FCGR, as shown in Figure 14 [17].

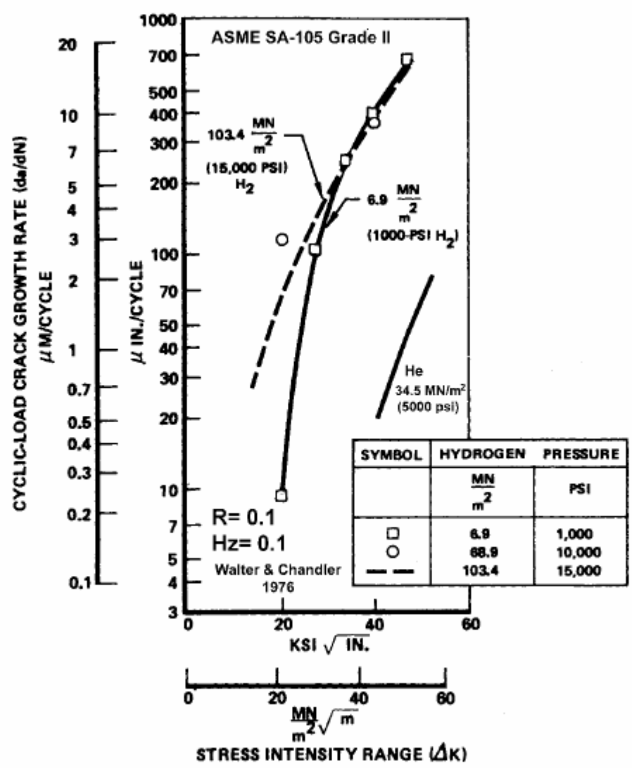


Figure 14**.** FCGR vs. stress intensity for SA-105 steel at 6.9 and 103.4 MPa [17]

The differences in test results regarding the influence of hydrogen pressure are difficult to resolve based on the available data. Several authors [10, 11, and 15] have noted the need for more information on the high pressure HE effects during fatigue processes. Some alloys, such as A-286, have demonstrated resistance during low cycle fatigue in both fracture mechanics and disk tests, but other results have also been reported in which this metal demonstrated high levels of embrittlement [10]. Many other alloys have not been tested for embrittlement in fatigue.

4.0 EFFECTS OF HYDROGEN PURITY

Several literature sources have reported the effects on hydrogen embrittlement of gaseous impurities. It is a well-known fact that higher levels of hydrogen purity lead to higher embrittling effects on steels, but it may also be valuable for high pressure storage purposes to know what gases act as inhibitors to HE. The results from relevant data sources are provided within this section.

Gas impurities can inhibit, accelerate, or have no effect upon hydrogen embrittlement. Disk permeation tests, in addition to the usual tests for HE, are useful to study the absorption of hydrogen with impurities present. H. Barthélémy and G.M. Pressouyre [1] described O_2 and SO_2 as inhibitors, CH_4 and N_2 as gases with no effect, and H_2S and CO_2 to be accelerators of HE. H_2O was listed as an impurity that could have either an inhibiting or accelerating effect. Reference 4 provided similar information, but also added that H_2S had also been found to decrease HE [4]. This, however, generally does not seem to be in line with findings from other sources.

Tests showed that HE effects decreased as oxygen content increased from 2 to 10,000 ppm, and also that higher strain rates led to higher inhibiting effects. Improved surface state of steel, however, meant less gas absorption, and thus decreased the inhibiting effect of oxygen [1].

C. San Marchi and B. Somerday [10] stated that oxygen, sulfur dioxide, and carbon monoxide lowered fatigue crack growth rate for X-42 steel in 6.9 MPa hydrogen to the value measured in nitrogen at 1.0 Hz. Furthermore, as shown in Figure 15, data is presented for two carbon steels showing the inhibiting effects of several gaseous mixtures at 6.9 MPa. Unlike previous results, however, a mixture containing hydrogen and CH_4 had lower fracture toughness than pure hydrogen, suggesting slight embrittlement by natural gas [10].

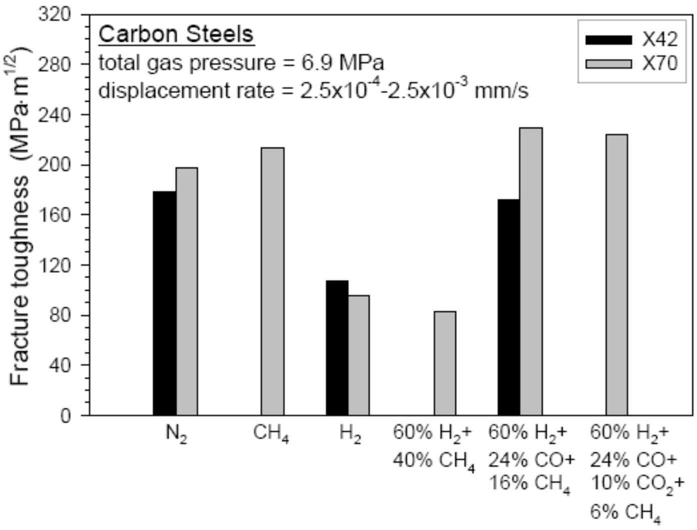


Figure 15. Fracture toughness vs. gas composition for two carbon steels [10]

The same authors presented data showing the inhibiting effects of O_2 and CO on fatigue crack growth for low alloy Cr-Mo steels at 1.1 MPa. Addition of H_20, CH_3SH, and H_2S accelerated FCGR, with the latter two additives demonstrating particularly detrimental effects. The results are provided in Figure 16 [10].

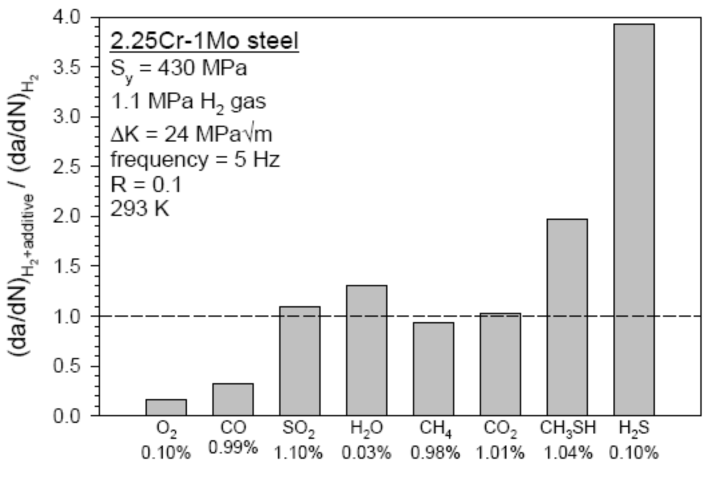
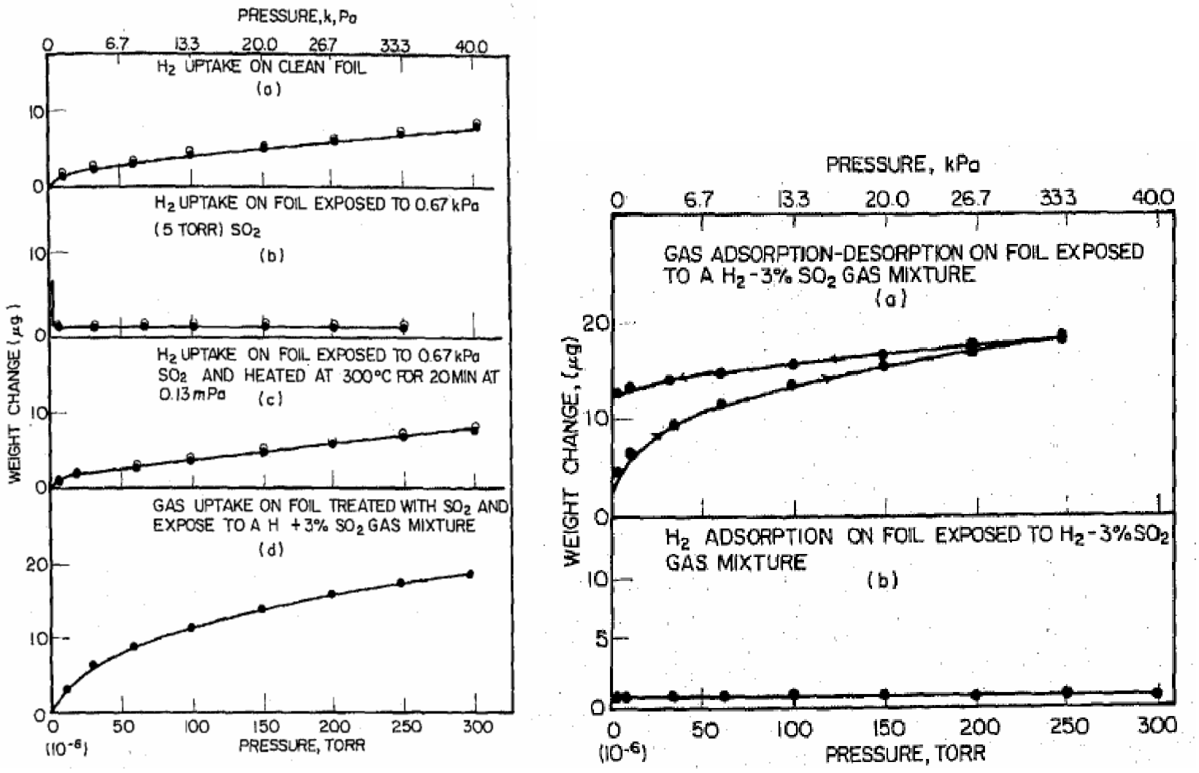


Figure 16: Ratio of FCGR with impurities to FCGR in pure hydrogen at fixed pressure and stress intensity range for a low-alloy ferritic steel [10]

Tests performed by P.J. Ficalora and V. Srikrishnan (1976) [16] studied the adsorption of hydrogen on iron foils at very low pressures (up to 0.4 MPa), as well as the influence of treatments with impurity gases. Pre-treatment of the foil with sulphur dioxide resulted in no hydrogen uptake, but hydrogen adsorption was restored after heat treatment at 300ºC for 20 min, meaning the SO_2 treatment did not present an irreversible solution. A gaseous mixture of hydrogen and 3% SO_2 led to high levels of gaseous adsorption, but later tests showed that the sulphur dioxide, and not the hydrogen, had preferentially adsorbed into the foil. See Figures 17 and 18, reproduced from Reference 16.

In similar tests, it was found that neither CO_2 nor N_2O affected hydrogen uptake in the foil. Pre-treatments with O_2 had no effect on hydrogen adsorption, but a gaseous mixture of oxygen and hydrogen retarded the uptake of the latter. Hydrogen sulphide accelerated hydrogen uptake because both H_2S and pure hydrogen were adsorbed by the foil, with a total quantity greater than the amount adsorbed in hydrogen gas alone [16].

Finally, D. Balch, C. San Marchi, and B. Somerday (2005) [7] presented crack extension data for H-11 steel for hydrogen and oxygen gas mixtures. The data clearly shows a stall in the crack growth for mixtures containing oxygen, thus illustrating the inhibiting effects of the gas on pure hydrogen. See Figure 19.



Figures 17 and 18. Gas adsorption properties of hydrogen and sulphur dioxide [16]

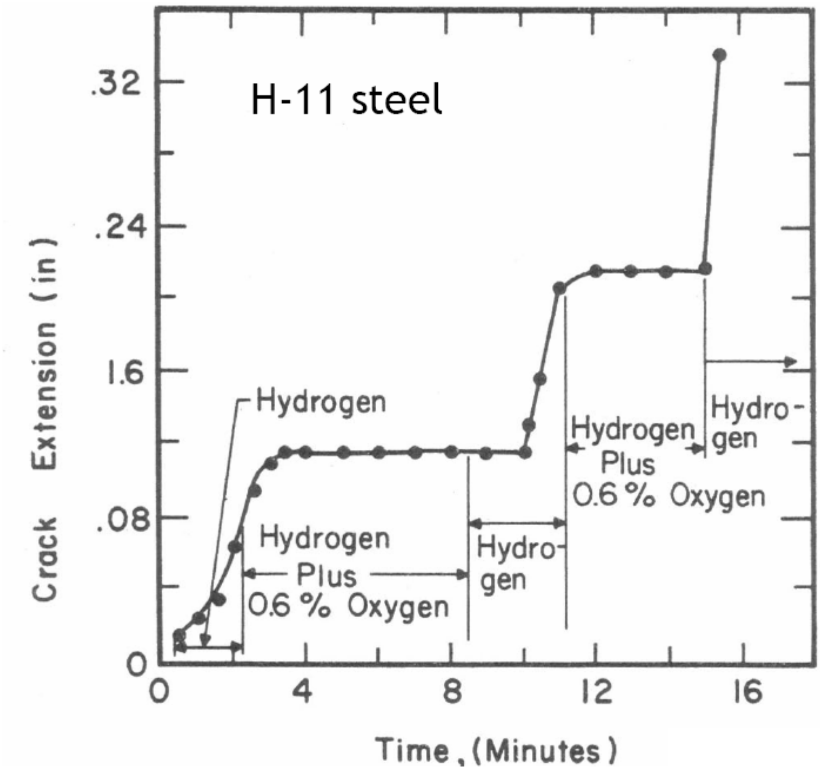


Figure 19. Crack extension vs. Time for hydrogen-oxygen mixtures [7]

5.0 EMBRITTLEMENT OF NON-STEELS

5.1 Aluminum

Aluminum and several Al alloys have demonstrated high resistance to HE in dry, gaseous environments, but high strength alloys have shown high susceptibility to stress-corrosion cracking in wet environments [10]. From the literature utilized in this study, the results of tensile tests in gaseous environments were available, but no results from fracture mechanics tests were reported.

C. San Marchi and B. Somerday presented data showing that the tensile properties of commercially pure aluminum, Al 1100 (99.0%), and high-purity aluminum (99.993%) were unaffected in hydrogen gas up to 34.5 and 52 MPa, respectively [10].

Ordin (1997) [18] presented results of tensile tests of notched specimens at 10,000 psi (68.9 MPa) in both helium and hydrogen for several aluminum alloys. Specimens of 7075-T73 experienced negligible embrittlement with only 2% loss of strength and 5% RAL. Alloys 6061-T6 and 1100 showed increases in strength compared to helium tests and no loss in %RA. Additionally, aluminum alloys 2011, 2024, and 6063 experienced no ductility losses, although strength values for these and 6061 were slightly lower in 10,000 psi hydrogen and helium as compared to properties at atmospheric pressure in air [18].

Under similar testing conditions (10,000 psi), pure titanium was listed as slightly embrittled because of 5% loss of strength, but there were no ductility losses. However, in Ti-6Al-4V and Ti-5Al-2.5Sn alloys, severe embrittlement occurred, thus demonstrating that titanium should probably be avoided as the base element in alloys with aluminum for hydrogen applications [18].

5.2 Copper

Copper, like aluminum, has very low hydrogen equilibrium solubility levels. Pure coppers have high levels of resistance to HE, but inclusions of oxygen in the material composition can significantly raise the level of susceptibility [10].

The reported hydrogen effects on copper properties during tensile testing vary. However, several sources [10, 18] presented results from a common set of tests in which smooth and notched specimens of OFHC (oxygen-free high conductivity) copper experienced no losses of strength or ductility in hydrogen pressure up to 69 MPa. Table 3 shows the results of smooth tensile tests for several coppers as reported in [10].

Table 3. Tensile properties of copper in high pressure hydrogen gas [10]

Material	Thermal precharging	Test environment	Strain rate (s^{-1})	S_y (MPa)	S_u (MPa)	El_u (%)	El_t (%)	RA (%)
Cold drawn, OFHC Cu	None	69 MPa He	—	269	290	—	20	94
	None	69 MPa H_2		—	283	—	20	94
Cu	None	Air	—	96	234	—	44	71
	(1)	Air		96	228	—	45	71
Annealed, OFHC Cu	None	Air	$2.1x10^{-6}$ m s^{-1}	117	193	—	57	84
	None	34.5 MPa He		83	193	—	63	85
	None	34.5 MPa H_2		76	186	—	63	84
OFHC Cu	None	Air	—	96.5	234	—	44	71
	None	69 MPa H_2		96.5	228	—	45	71
Boron deoxidized Cu	None	Air	—	96.5	234	—	40	92
	(2)	Air		55.2	200	—	49	92
	None	69 MPa H_2		68.9	214	—	46	94
	(2)	69 MPa H_2		41.4	200	—	51	96

(1) 69 MPa hydrogen, 428 K, 720 h: ~0.03 wppm hydrogen (<1 appm)
(2) 300 MPa hydrogen, 473 K, 1344 h

The low strength of copper has resulted in very little available data for fracture mechanics tests. Cu-Be was reported to perform well in the presence of hydrogen and have good mechanical properties [2], but no data was found within the acquired documents. The literature contained no fatigue data for copper, although it was reported [10] that hydrogen had no effect in disk rupture testing. For copper and its alloys it appears that more testing is necessary to completely understand the effects of hydrogen gas, particularly with regard to pressure.

6.0 CONCLUSIONS

A literature survey was conducted to find relevant information for testing methods of hydrogen embrittlement, as well as the effects of high pressure (from 700-1000 bar) and high purity hydrogen. It was found that the most common testing methods currently used to study HE are disk, tensile, and fracture mechanics tests. While data was readily available for most of these types of tests, there was a lack of information in the data, and thus a need for further study, on the fatigue effects of high pressure hydrogen. Additionally, while most resources presented similar information about the effects of impurities on hydrogen embrittlement, almost all available data was from low-pressure tests. In the future, it may be helpful if tests are performed to study the effects of impurities at higher pressures as well.

The embrittling effects of hydrogen as pressure increased were generally found to increase as well, but the results vary significantly depending on the material. Some high yield strength steels have demonstrated cracking threshold values that reach a limit at about 60 MPa. If pressures are increased from the current 100-200 bar range to a value of 700 bars, these high yield strength steels could pose a risk if used for hydrogen storage. In order to minimize risk, austenitic steels are currently one of the safest options. It remains unclear whether a threshold pressure value (beyond which properties become pressure-independent) exists, although this was seen in a few of the steels studied. This characteristic should be examined for steels that appear to be good candidates for high pressure hydrogen storage. In particular, types 316 and A286 have demonstrated successful behavior during testing in hydrogen environments at pressures near 700 bar. In addition to studies needed to determine a threshold pressure for these steels, more extensive fatigue testing is needed to ensure safety, as this is the best method of simulating the cyclic stresses of a pressurized storage vessel.

The effects of impurities as published in open literature were also studied to determine the role of hydrogen purity in HE. The results were almost unanimous in showing that oxygen acts as an inhibitor to embrittlement while H_2S acts as an accelerator. For other types of impurities, however, the effects on HE were somewhat unclear and varied. Results for H_20, which would be one of the most likely impurities to be found in storage vessels, showed slight embrittling effects. Because the effect was generally very low, it is unlikely that this would pose a significant problem in standard operation, but testing is necessary to confirm that low levels of H_2O are allowable without posing safety risks.

Although the study focused primarily on hydrogen embrittlement of steels, it was found that aluminum and its alloys have demonstrated high resistance to HE. Aluminum alloys showed almost no decrease in ductility, but they have demonstrated some losses of strength in high pressure hydrogen. It is strongly recommended that research be performed to improve the understanding of aluminum behavior in hydrogen, particularly through high pressure fatigue and fracture mechanics testing. Impurities such as H_20 could cause difficulties for aluminum, however, with its susceptibility to stress corrosion cracking in wet environments. Similar testing should be performed for copper and its alloys, as these materials have also performed well in high pressure hydrogen. It appears that, given their performance at high pressures, these types of metals would not experience severe degradation of properties at 700 bar, but this is not certain without more extensive study.

REFERENCES

1. Barthélémy, H. and Pressouyre, G.M., Hydrogen Gas Embrittlement of Steels: Synthesis of the CEC hydrogen energy program (1975-1983). Commission of the European Communities, 1985.
2. Barthélémy, H., Compatibility of Metallic Materials with Hydrogen. Air Liquide.
3. Barthélémy, H., Hydrogen Equipment: Safety and Design Issues. Critical Equipment Validation Seminar, 2008.
4. Barthélémy, H., How to Select Steels for Compressed and Liquefied Hydrogen Equipment. 1989.
5. Pressouyre, G.M., Current Solutions to Hydrogen Problems in Steel, ed. by Interrante C.G. and Pressouyre G.M., Proceedings of the First International Conference on Current Solutions to Hydrogen Problems in Steels, November 1 (1982), pp. 18-31.
6. Gutierrez-Solana, F. and Elices, M., High Pressure Hydrogen Behavior of a Pipeline Steel, ed. by Interrante, C.G. and Pressouyre, G.M., Proceedings of the First International Conference on Current Solutions to Hydrogen Problems in Steels, November 1 (1982), pp. 181-185.

7. Balch, D., San Marchi, C., and Somerday, B., Hydrogen-Assisted Fracture: Materials Testing and Variables Governing Fracture. Sandia National Laboratories. Hydrogen Pipeline Working Group Workshop, August 30-31, 2005.
8. Xu, K., Properties of Line pipe Steels in High Pressure Hydrogen. Praxair, Inc, Materials Engineering Laboratory. ASTM G1 H2 Workshop, May 17 2005.
9. Somerday, B., Materials Compatibility, Sandia National Laboratories. May 17, 2007.
10. San Marchi, C. and Somerday, B., Technical Reference on Hydrogen Compatibility of Materials. Sandia National Laboratories, March 2008.
11. Barbier, F., Compatibility of Materials with Gaseous Hydrogen. Air Liquide, H_2 Energy R&D. February 12, 2008.
12. Barthélémy, H. and Wastiaux, S., Hydrogen compatibility tests with metallic materials. According to ISO 111114-4: New test results using method C. Air Liquide, March 2006.
13. Rana, M., Development of ASME Code Rules for 15,000 PSI Hydrogen Vessels. Hydrogen Gas Embrittlement Workshop, ASTM Meeting, May 17, 2005.
14. Adams, T. and Sindelair, R., SRNL Research on Hydrogen Effects on Materials; Past, Present, and Future. Hydrogen Gas Embrittlement Workshop, ASTM Meeting, May 17, 2005.
15. Slusser, J., Selecting Metals for High Pressure Hydrogen Service. Hydrogen Gas Embrittlement Workshop, ASTM Meeting, May 17, 2005.
16. Srikrishnan, V. and Ficalora, P.J., The Role of Gaseous Impurities in Hydrogen Embrittlement of Steel. September 7, 1976.
17. Lam, P.S., Sindelar, R.L. and Adams, T.M., Literature Survey of Gaseous Hydrogen Effects on the Mechanical Properties of Carbon and Low Alloy Steels. Savannah River National Laboratory, ASME Pressure Vessels and Piping Division Conference, 22 July 2007.
18. Ordin, P. M., Safety Standard for Hydrogen and Hydrogen Systems. Guidelines for hydrogen system design, materials selection, operations, storage, and transportation. NASA, 1997.
19. Moody, N. R., Robinson, S.L. and Somerday B.P., Hydrogen Embrittlement of Stainless Steels, Sandia National Laboratories, Livermore, CA.
20. ISO 11114-4: Transportable gas cylinders, compatibility of cylinder and valve materials with gas contents, 2006.
21. Barthélémy, H., Hydrogen gas embrittlement of some austenitic stainless steels. Hydrogen and Materials, May 9-13, 1988.
22. Lynch, S. P. and Ryan, N.E., Mechanisms of hydrogen embrittlement- Crack growth in a low alloy ultra-high-strength steel under cyclic and sustained stresses in gaseous hydrogen. Second International Congress on Hydrogen in Metals, 1977.