HYDROGEN IMPACT ON FRACTURE PROPERTIES OF 34CrMo4 PRESSURE CYLINDER STEEL

[1]Marek DOBIÁŠ, [1]Petr ČÍŽEK, [1]Ladislav KANDER, [1]Petr JONŠTA

[1]MATERIÁLOVÝ A METALURGICKÝ VÝZKUM s.r.o., Ostrava, Czech Republic, EU, marek.dobias@mmvyzkum.cz

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Abstract

Currently, technological development is focused, among other things, on hydrogen and its technologies. Hydrogen storage must be very well secured and material resistance against hydrogen embrittlement is tested using different approaches. Nevertheless, there are three specified methods listed in EN ISO 11114-4 standard, which are disc test, fracture mechanic test and test method to determine the resistance to hydrogen assisted cracking of steel cylinders. Many works showed differences in results evaluated from latter and last method, eventually method for measurement of fracture toughness. Thus, rising crack opening test according to EN ISO 12135 standard, and last method stated in EN ISO 11114-4, i.e., constant displacement test, were done in this paper to find out, how hydrogen damages steel mentioned above. This paper aims on chromium molybdenum steel 34CrMo4, which is often used for production of metal pressure cylinders. Compact tension specimens, respectively modified compact tension specimens with central hole, were prepared and tested for fracture toughness measurement in air and in high-pressure hydrogen gas at 30 MPa, respectively for latter method.

Keywords: Hydrogen embrittlement, fracture toughness, pressure cylinders, 34CrMo4 steel

1. INTRODUCTION

Contemporary requirements on better storage conditions of pressure cylinders need materials of higher quality, which increase service life of pressure cylinders. Subcritical cracking threshold measured under quasi-static loading in high-pressure hydrogen is necessary input to calculate life prediction assessment. Constant displacement test, which can be done according to EN ISO 11114-4 [1], method C or both ASME BPVC VIII-3 KD-10 [2] and ASTM E1681 [3], and rising crack opening test, which can be done according to ASTM E1820 [4], EN ISO 11114-4 [1], method B or EN ISO 12135 [5], can yield, among another tests, this threshold. EN ISO 11114-4 [1] standard was applied for first mentioned test and EN ISO 12135 [5] standard was applied for latter test. Nevertheless, application of these tests on lower-strength steels often shows different results. Tests on low strength 34CrMo4 steel, which is widely used for pressure cylinders, was used for testing in high-pressure hydrogen gas at 30 MPa and in air for comparison to gain some data for their evaluation [6].

2. MATERIAL PROPERTIES

Results of chemical analysis are compared with standard values in **Table 1**.

Table 1 Chemical analysis and standard values in (wt%)

Element	C	Si	Mn	P	S	Cr	Cu	Mo
EN ISO 683-2 [7]	0.30-0.37	0.10-0.40	0.60-0.90	≤0.025	≤0.035	0.90-1.20	≤0.40	0.15-0.30
Chemical analysis [8]	0.35	0.302	0.78	0.003	<0.001	1.13	0.114	0.203

Measured values are in agreement with standard. Tensile tests were provided on three longitudinal specimens with diameter of 10.01 mm in air environment at ambient temperature. Average values are 830 MPa for ultimate tensile strength, σ_{UTS}, and 661 MPa for 0.2 % yield strength, $\sigma_{0.2}$.

3. APPARATUS

Apparatus, as can be seen in **Figure 1**, was used for tests in high-pressure hydrogen environment. Volume of both autoclaves is 0.552 dm^3. Both plunger and dynamic autoclave are made to be attached to servohydraulic testing machines, moreover, dynamic autoclave can be used also as static. This dynamic autoclave was developed and patented by MMV. Used hydrogen gas with purity of 5N5 was pressurized to 30 MPa with help of plunger because of lower pressure in pressure cylinder. Procedure of pressurizing was as follows: scavenging with nitrogen gas through R4 valve, vacuum pumping and pressurizing with hydrogen gas to required pressure.

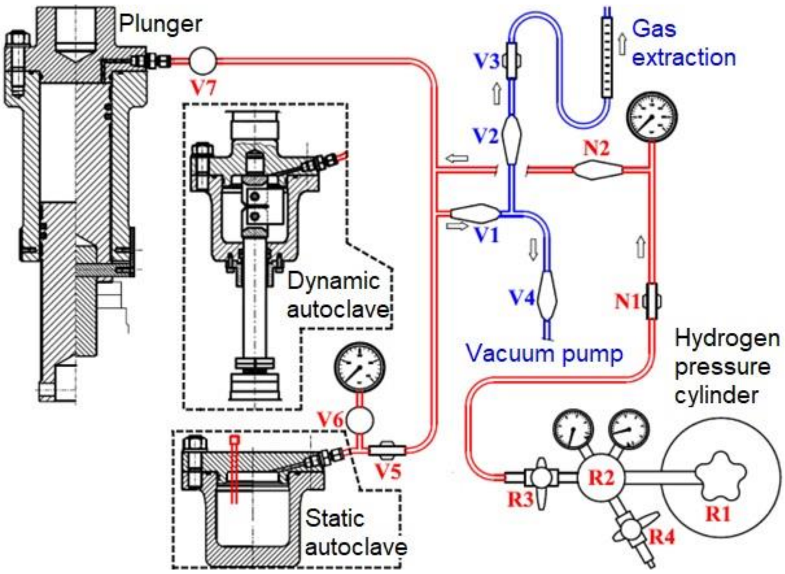

Figure 1 Apparatus for hydrogen environment

4. RISING CRACK OPENING TEST

Rising crack opening test was conducted according to EN ISO 12135 [5] so that the result was J-R curve. Five 0.5T-C(T) specimens with dimensions showed in **Figure 2 a)** were fabricated, precracked at maximum stress intensity factor K_{MAX} = 28 MPa·$m^{0.5}$ and stress ratio R = 0.1 and subsequently tested. Testing rate was $5 \cdot 10^{-3}$ mm·s^{-1}. Unloaded specimens were heat tinted and broken with aid of liquid nitrogen. Measured values of crack length were used for obtaining the crack initiation threshold stress intensity factor $K_{JC0.2}$ value of 206.47 MPa·$m^{0.5}$, which was calculated according to equation (1) [5] from corresponding fracture resistance at 0.2 mm crack growth including blunting, $J_{0.2}$.

$$K_{JC0.2} = \sqrt{\frac{J_{0.2} \cdot E}{(1-\nu)^2}} \tag{1}$$

where:

$K_{JC0.2}$ - the equivalent fracture toughness (MPa·$m^{0.5}$)

$J_{0.2}$ - fracture resistance at 0.2 mm crack growth including blunting (kJ·m^{-2})

E - Young's modulus (MPa)

ν - Poisson's ratio (-) [5]

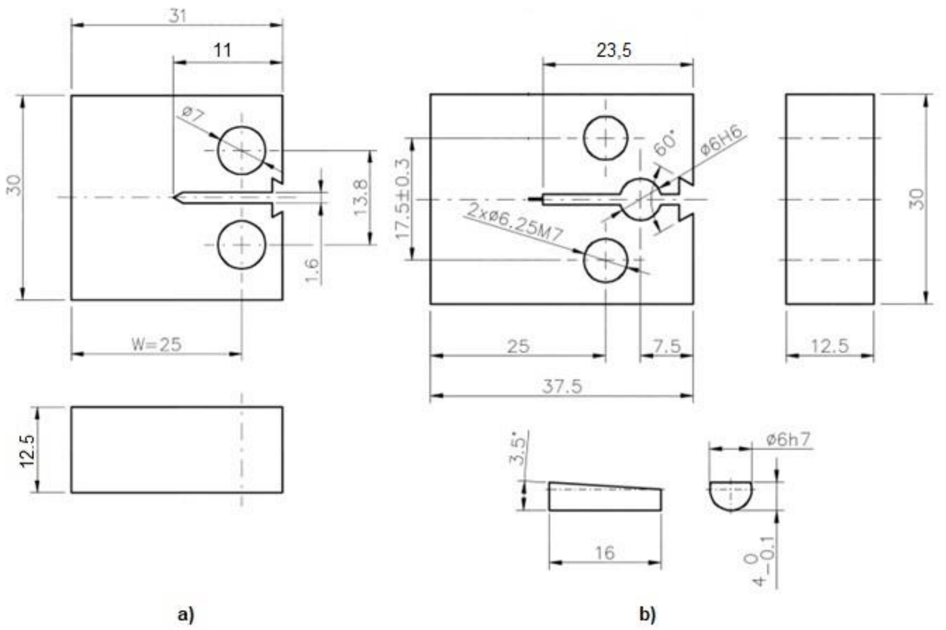

Figure 2 Specimen 0.5T-C(T) for a) rising crack opening test, b) constant displacement test

Another set of five 0.5T-C(T) specimens were used for rising crack opening test in high-pressure hydrogen environment. Precracking was done according to conditions above mentioned and tests were conducted without extensometer for crack mouth opening displacement measurement, due to limited space in autoclave and due to its impropriety for measuring in hydrogen environment, so in this case, crack tip opening displacement δ_0 was calculated thanks to algebraic difference of notch opening displacement V before and after test, which is equivalent to plastic component V_p, measured under microscope. Testing rate was $2{\cdot}10^{-4}$ mm·s^{-1}. The remaining steps are same as above. CTOD δ_0 was converted to fracture resistance J_0 according to approximated equation (2) [5].

$$J_0 = 2 \cdot \sigma_{0.2} \cdot \delta_0 \tag{2}$$

Resulting value of crack initiation threshold stress intensity factor $K_{JC0.2}$ is 147.68 MPa·m$^{0.5}$. Dependence of fracture resistance J_0 on crack extension Δa is in **Figure 3**. All specimens met plane strain criteria in conformity with equation (3) [9].

$$a,\ B \geq 2.5 \cdot \left(\frac{K_I}{\sigma_{0.2}}\right)^2 \tag{3}$$

where:

K_I - fracture toughness (MPa·m$^{0.5}$)

a – crack length (mm)

B - thickness (mm)

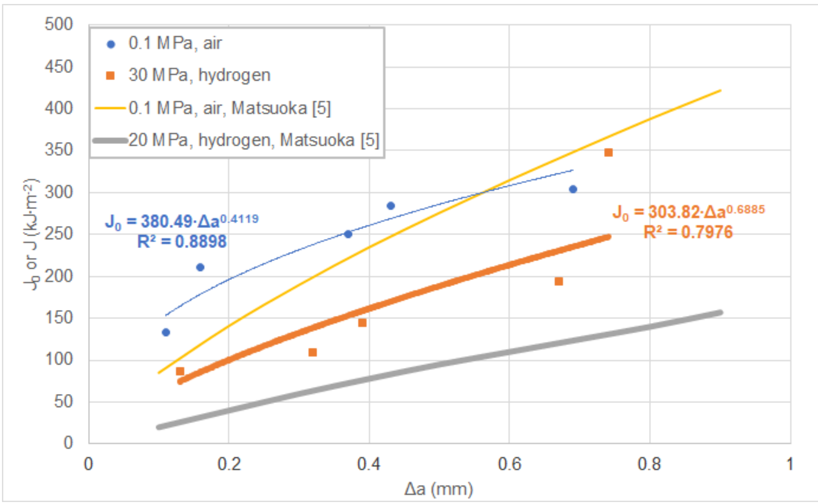

Figure 3 J_0 – Δa plot

5. CONSTANT DISPLACEMENT TEST

Constant displacement test was done according to method C, mentioned in EN ISO 11114-4 [1], i.e., test method to determine the resistance to hydrogen assisted cracking of steel cylinders. Three modified 0.5T-C(T) specimens of the Y-X orientation, see **Figure 2b)**, were machined with center hole serving for fixing static load with help of two wedges. Precracking conditions were same as above. Then specimens were loaded to constant displacement computed from applied elastic stress intensity factor K_{IAPP} = 78.61 MPa·m$^{0.5}$, which was calculated according to equation (4) [1], fixed with wedges, placed in static autoclave and tested for 1,000 hours.

$$K_{IAPP} = 1.5 \cdot 60 \cdot \frac{R_m}{950} \tag{4}$$

Specimens were broken after the test and crack extension Δa was measured as noted above. Resulting value of threshold fracture toughness was equal to K_{IAPP} due to no crack extension, except one specimen having crack extension $\Delta a \approx$ 15 μm.

6. FRACTOGRAPHY

Fractures of specimens were examinated by scanning electron microscope in the mode of back scattered electrons. Specimen after constant displacement test is in **Figure 4 a)**, where border between precrack and final fracture can be seen and in **Figure 4 b)**, where detail of stable crack growth with quasi-cleavage type of fracture is. Specimen after rising crack opening test in air is in **Figure 5 a)** and in 30 MPa hydrogen gas in **Figure 5 b)**, both shows ductile fracture.

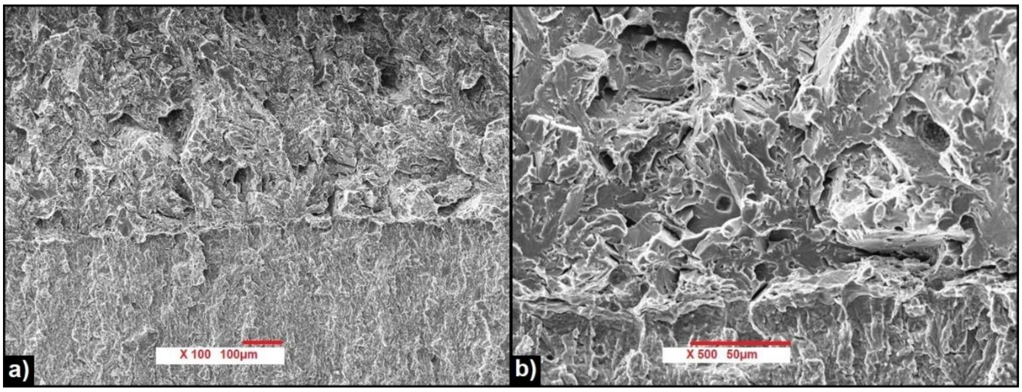

Figure 4 SEM images of specimen after constant displacement test: a) border between precrack (bottom) and final fracture (top), b) detail of stable crack growth

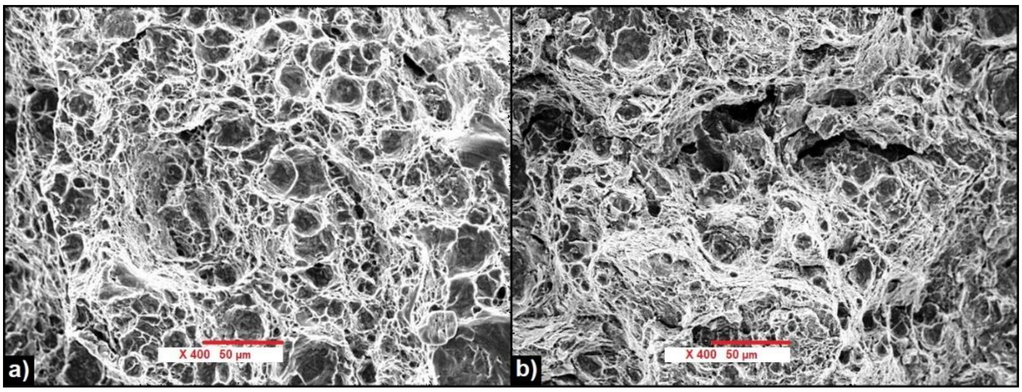

Figure 5 SEM images of crack extension area of specimens: a) after rising crack opening test: in air and b) in 30 MPa hydrogen gas

7. DISSCUSION

It is unusual according to trend, e.g. works of Matsumoto et al. [10] and Nibur et al. [6], that rising crack opening test shows almost two times higher value of crack initiation threshold stress intensity factor $K_{JC0.2}$ than threshold stress intensity factor $K_{I,H}$ of constant displacement test.

Previous work by Čížek and Kander [11], where method B was carried out on 34CrMo4 steel with the ultimate tensile strength σ_{UTS} around 1000 MPa in 30 MPa hydrogen gas, showed results of threshold stress intensity factor $K_{I,H}$ range from 40.5 to 94.3 MPa·m$^{0.5}$. These values are lower than ours apparently due to higher tensile strength.

Matsuoka et al. [12,13] done several tests on JIS-SCM435 pressure cylinder steel, which is equivalent to 34CrMo4 steel, with σ_{UTS} = 824 MPa and $\sigma_{0.2}$ = 687 MPa. Value of threshold fracture toughness $K_{I,H}$ gained from elasto-plastic fracture toughness test according to ASTM E1820 [4] in 20 MPa hydrogen gas was two thirds lower than our value, see *J*-integral dependance on crack extension Δa in **Figure 3**. However, they used L-R oriented specimens with width W = 50.8 mm, which can exhibit different behavior in hydrogen gas. Calculated value of threshold fracture toughness $K_{I,H}$ from polynomial curve for constant displacement test done according to ASME BPVC VIII-3 KD-10 [2] on was 118.6 MPa·m$^{0.5}$, which is higher than our value. They also provided fatigue crack growth rate tests, which proved ductile crack appearance for steels with ultimate tensile strength $\sigma_{UTS} \leq$ 900 MPa, that is in agreement with our result of ductile fracture in specimens after rising crack opening test.

8. CONCLUSION

Rising crack opening test and constant displacement test were done on specimens made of 34CrMo4 steel. First mentioned test showed decrease of fracture resistance K_{JC} due to hydrogen impact. Latter test showed no crack extension except one with stable crack growth $\Delta a \approx$ 15 µm. These data can be used for future testing.

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