EFFECT OF HIGH PRESSURE HYDROGEN ENVIRONMENT ON FATIGUE CRACK GROWTH RATE PROPERTIES OF STRUCTURAL STEEL USED FOR CYLINDERS

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Abstract

Paper deals with evaluation of effect of high pressure hydrogen environment with actual pressure of hydrogen up to 30 MPa on fatigue crack growth rate properties of structural steel used for cylinders production. 34CrNiMo6 grade steel was used for experimental programme. A unique new testing equipment (hydrogen autoclave) was built in MATERIAL & METALLURGICAL RESEARCH, Ltd. to study degradation mechanism of high pressure hydrogen environment on mechanical properties including fracture mechanics properties of structural materials. There is comparison of results of crack growth rate in the air and high pressure hydrogen presented in the paper. Potential method was used for crack growth monitoring in the hydrogen autoclave due to cycling. Effect of hydrogen is presented on fractography examination, change in fracture morphology was found on fracture surfaces of tested specimens due to presence of high pressure hydrogen.

Keywords: High pressure hydrogen environment, fracture mechanics, cylinders, 34CrNiMo6 steel

1. INTRODUCTION

This paper presents a short review of information and data from research programme concerned with the influence of high pressure hydrogen environment on fatigue crack growth properties of steel used for cylinders and gas containment. Although 34CrNiMo6 grade steel (W.N. 1.6582) has been used for many years for the storage of hydrogen without major problems, some failures have been reported in recent years [1,2]. Failure has usually been associated with the development of circumferential cracks initiated from small manufacturing defects on the inner surface of the cylinder, close to the point where the relatively thin, parallel sided wall joins the thicker concave base. It is known that 34CrNiMo6 steel shows some susceptibility to hydrogen induced crack growth under static load, but there are only a few laboratories in Europe that are able to carry out dynamic tests under high pressure hydrogen. This report reviews method and equipment originally developed in MATERIAL & METALLURGICAL RESEARCH, Ltd for testing of material resistance against high pressure hydrogen up to pressure 30 MPa using fracture mechanics type of the specimens and monitoring fatigue crack growth properties.

2. MATERIAL, EQUIPMENT, TEST METHOD

For investigation has been used commercial cylinder manufactured from 34CrNiMo6 steel. Basic chemical composition of the steel under investigation is given in the **Table 1**.

Table 1 Chemical composition of 34CrNiMo6 steel [wt. %]

C	Si	Mn	P	S	Cr	Mo	Ni
0.30	max.	0.50	max.	max.	1.30	0.15	1.30
0.38	0.40	0.80	0.025	0.035	1.50	0.30	1.70

Fatigue crack growth properties were measured using longitudinal compact tension test pieces machined from cylinders according to **Figure 1**.

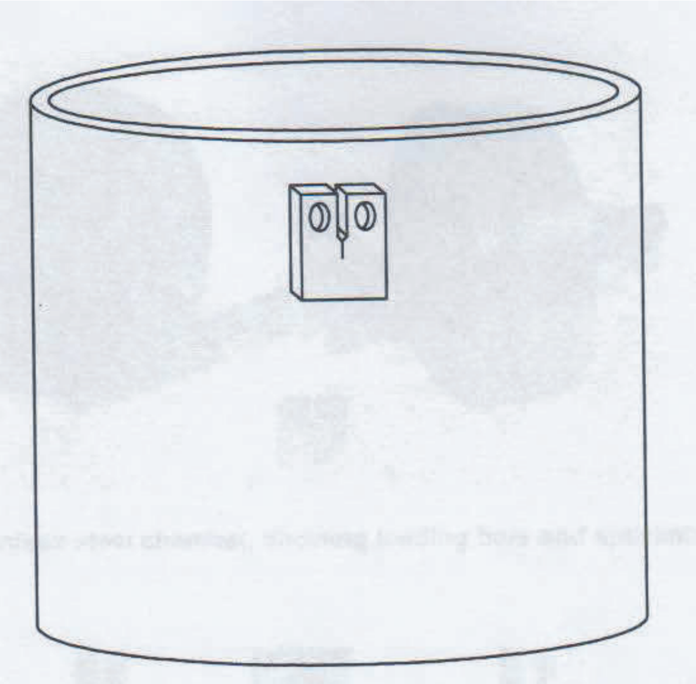

Figure 1 Orientation of CT specimens [2]

All crack growth rate tests were performed in accordance with the testing and evaluation procedures laid down in ASTM E 647. Fatigue crack growth rate tests were performed in special hydrogen autoclave manufactured from stainless steel originally developed in our company. Hydrogen autoclave was installed on servomechanical testing machine MTS 100 kN used in this testing programme.

All test pieces were fatigue precracked in the air at a frequency of approximately 15 Hz using a value of maximum load below that to be used in subsequent test. This procedure was used to produce a fatigue crack approximately 1.5 mm long and consequently reduced the time needed to initiate cracking during the tests.

When the test specimen was installed into hydrogen autoclave, rotary pump was used to evacuate to a pressure below 1 Pa prior to the introduction of the gaseous environment. The tests in the hydrogen were conducted at pressure 15 MPa and at frequency 7 Hz. These tests used a sine waveform and stress ratio 0.63. This value was chosen to simulate the effects of service refilling as closely as possible in the prevailing circumstances.

Throughout each test the crack length was continuously monitored using the ACPD method. Calibration curve for ACPD method for 1/2CT specimens is shown in the **Figure 2**. It can be clearly seen, that calibration curve and ACPD method give good results if the crack length is between 11 and 17 mm, which corresponds to crack ratio a/W between 0.4 and 0.7. Maximum value of stress intensity factor during the cyclic loading was K_{max} = 27 MPam^{0,5}. This value corresponds to maximum circumferential stress in the wall thickness from numerical simulation see **Figure 3** [3]. The first aim of the testing programme was to simulate the situation at which small manufacture defect appears in the cylinder and after expected minimum lifetime that corresponds to 50 000 cycles such defect is not able to moving during cycling at high pressure hydrogen. The second step was to verify maximum expected lifetime that corresponds to 150 000 cycles at pressure ratio between 95% and 60 % maximum working pressure (R = 0.63).

Third part of our testing programme was to evaluate number of cycles at which crack will grow on 1,5 mm. Such situation corresponds to the real situation at which small manufacturing defects on the inner surface of the cylinder can grow during the working period up to maximum permissible length.

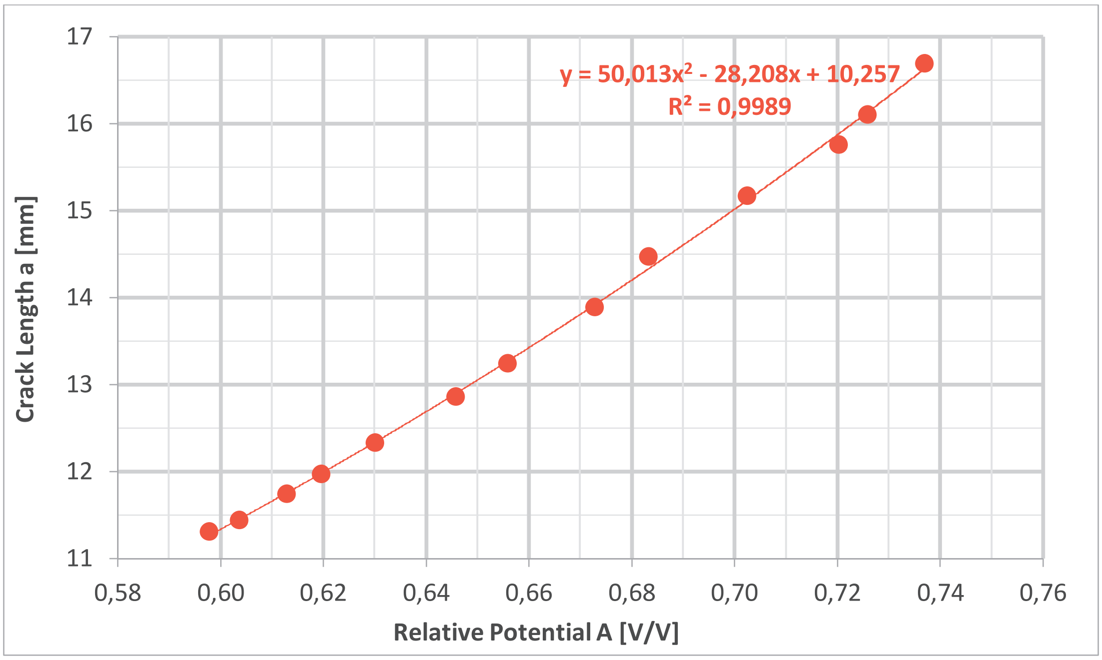

Figure 2 Calibration curve ACPD method for CT specimens

After testing in high pressure autoclave several specimens were chosen for examination using a scanning electron microscope.

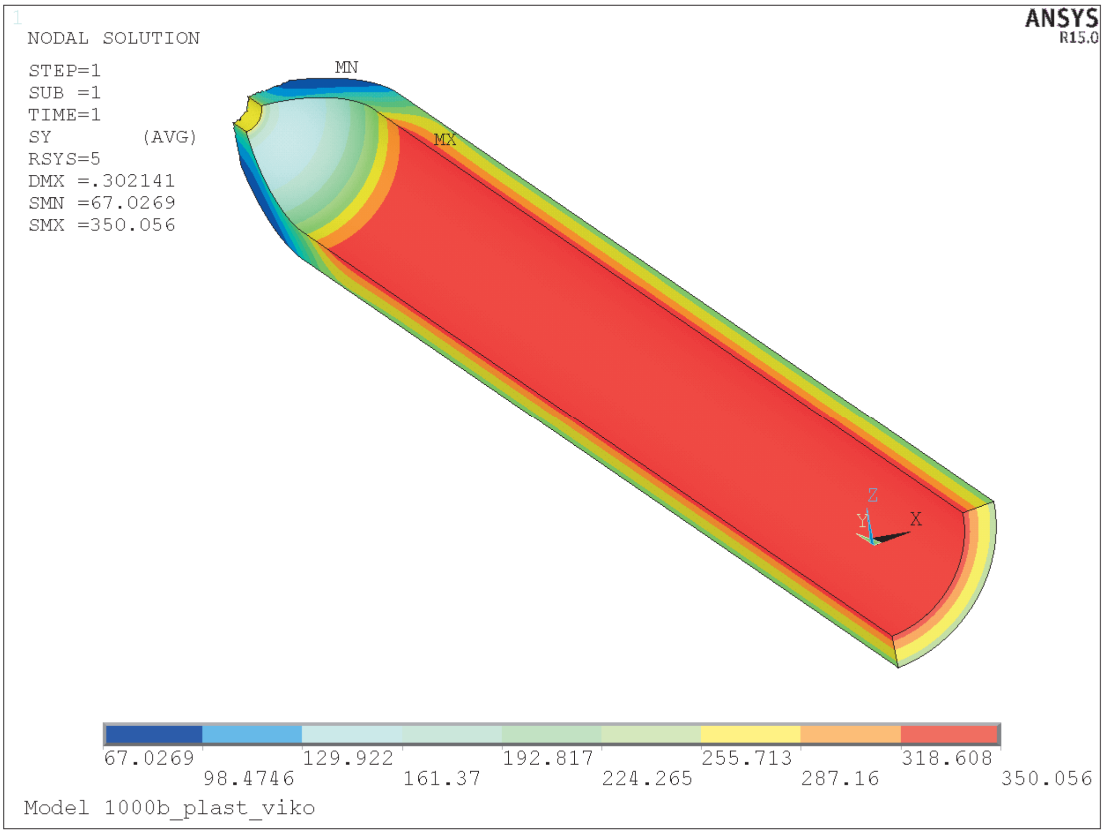

Figure 3 Numerical simulation of stress distribution [3]

3. TEST RESULTS

Table 2 summarizes all tests conducted in high pressure hydrogen with 34CrNiMo6 steel during the steps 1 and 2. Three specimens were tested in step one and two in accordance with ISO 11114-4 standard with hydrogen pressure 15 MPa. Maximum circumferential stress in real cylinder was calculated using FEM method and was found to be P_{max} = 346 MPa [4]. which corresponds to a maximum value of stress intensity factor K_{max} = 27 MPam$^{1/2}$. R ratio evaluated as the minimum loading divided maximum loading was R = 0.63. Stress intensity factor range was calculated to be ΔK = 9.5 MPam$^{1/2}$ and the test frequency was 7 Hz.

Table 2 Test results for step 1 and step 2.

Specimen ID	Thickness	Width	Crack length at the start	Crack length at the end	Number of cycles	Note
	B	W	a_0	a_t	N	
	(mm)	(mm)	(mm)	(mm)	(1)	
L8	12.5	25.0	10.96/10.83	10.96/10.83	50 000	not failed
L9			11.10/11.15	11.10/11.15	50 000	not failed
L10			11.13/11.20	11.13/11.20	50 000	not failed
L11	12.5	25.0	11.30/11.30	11.52/11.47	150 000	not failed
L13			11.25/11.55	11.38/11.76	150 000	not failed
L14			11.10/11.10	11.29/11.22	150 000	not failed

Table 3 summarizes the crack growth rate measurement test conducted in high pressure hydrogen with 34CrNiMo6 steel during the step 3. One specimen was tested in step three with the same above mentioned conditions. from the **Table 3** can be seen that crack needs about 200 000 cycles at given loading to growth 1.5 mm in length. Even after such number of cycles specimen brittle fracture was not observed and specimen was not failed in two parts.

Table 3 Test results for step 3.

Specimen ID	Thickness	Width	Average crack length at the start	Average crack length at the end	Number of cycles	Note
	B	W	a_0	a_t	N	
	(mm)	(mm)	(mm)	(mm)	(1)	
L16	12.5	25.0	11.48	12.98	192 528	not failed

Fractographic examination was used to identify fracture mechanism of crack propagation in high pressure hydrogen environment of the steel under investigation. Fractography examination was performed on fracture surfaces of the specimen L16 after where significant crack growth, identified using ACPD method, has been found after nearly 200 000 cycles, see **Table 3**. After end of the cyclic in high pressure hydrogen test specimens was broken in liquid nitrogen to minimize plastic deformation and fracture surfaces was preserved using alcohol. Fractography analysis was performed on scanning electron microscope JEOL-JSM 5510 and results are presented in the **Figures 4-6**.

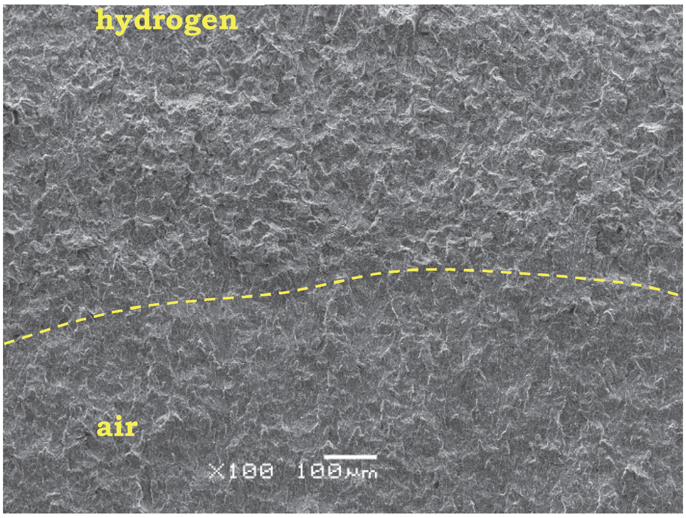

Figure 4 Fracture surface, interface between air (precracking) and hydrogen (testing)

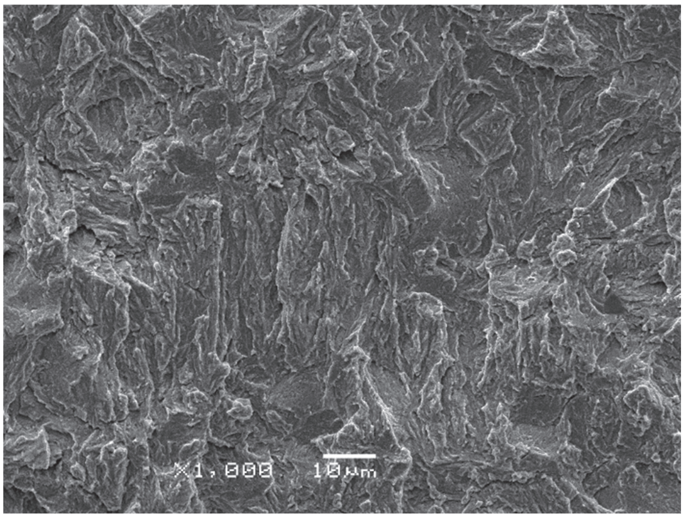

Figure 5 Detail of fracture surface precracked in air

Figure 4 shows visible differences between area precracked in air during preparation of the fatigue crack and following are originated from testing in high pressure hydrogen environment, details of both areas observed using high magnification are shown in the **Figures 5** and **6**. Change of fracture mechanism from transgranular cleavage to intergranular fracture due to hydrogen embrittlement can be clearly identified.

4. DISCUSSION

Effect of high pressure hydrogen on crack growth rate of the structural steels is highly monitored material characteristic especially in the case om materials used for cylinders manufacturing. Hydrogen affects fracture and fatigue behaviour of bcc metals significantly especially in the case of martensitic structure. Nevertheless, experimental work shows high resistance steel under investigation under hydrogen degradation. Crack growth rate in the hydrogen was evaluated and even after nearly 200 000 cycles (which is 5x times greater lifetime compare with calculated value) neither significant crack growth nor brittle fracture failure was observed. Change in fracture mechanisms was observed on the fracture surfaces due to hydrogen, see results of fractographic analysis (**Figures 4-6**) which can be taken as an evidence of good practice of the experiments and verification of capability to carry out such test in new developed high pressure hydrogen autoclave. Further work is continuing focused on effect of R ratio on crack growth rate in hydrogen environment.

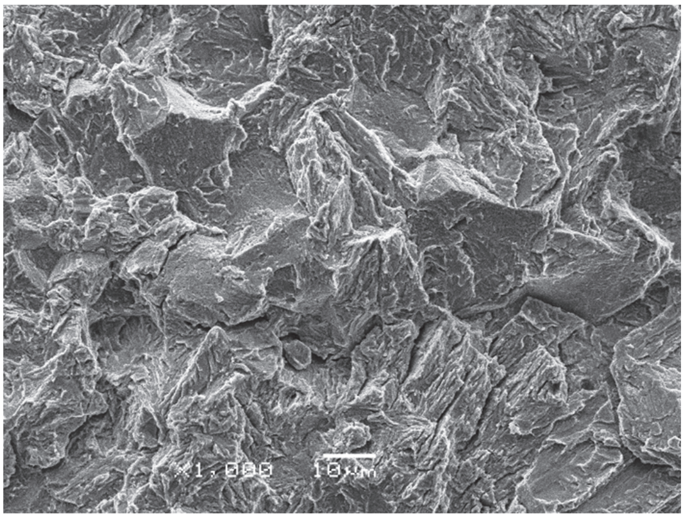

Figure 6 Detail of fracture surface tested in high pressure hydrogen

5. CONCLUSION

Paper summarizes results of work with new test technique for quantification of effect of high pressure hydrogen environment on material properties especially on fatigue crack growth rate. As there is no other similar experimental equipment for such type of testing in the Czech Republic, we try in this paper to show both ability and first achieved results of this field. Because hydrogen cylinders production is growing and hydrogen as a potential resource of energy for the future is expected, knowledge about fracture and fatigue behavior of many types of structural materials will be needed soon. We are continuing our study of high pressure hydrogen degradation of fracture and fatigue properties of structural materials included both of steels as well as other materials.

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