FRACTURE MECHANICS OF STEELS IN HYDROGEN ENVIRONMENT

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ABSTRACT

A fast, accurate and reproducible technique for the determination of fracture mechanics parameters of steel in high pressure hydrogen environment is described. Parameters under study are steel grade and mechanical characteristics, pressure and loading mode, i.e. static loading or fatigue.

KEYWORDS

Hydrogen embrittlement. Fracture mechanics. Fatigue. High pressure. Threshold stress intensity factor. Crack growth rate.

INTRODUCTION

The increasing use of materials in hydrogen containing or producing environments, makes hydrogen embrittlement a very up to date problem. To characterize a steel's susceptibility to such an environment, a broad range of techniques is currently being used in laboratories throughout the world. Among all techniques, fracture mechanics testing is very attractive due to its solid fundamental basis ; thus, such important values as crack growth rate in hydrogen or permissible stresses or crack lengths, may be calculated. This paper describes a technique that makes use of fracture mechanics concepts, and offers at the same time reliability and fast obtention of critical data.

EXPERIMENTAL PROCEDURE

Specimens

Wedge-opening-load (WOL - 1 or 2 T) specimens, with width W = 6.40 cm or W = 12.80 cm, thickness B = 2.5 cm or B = 5.0 cm, and half-height to width ratio = 0.486, have been used. WOL - 2 T specimens were occasionnally used when the yield stress, σ_y, of the material was low, so as to satisfy ASTM conditions for plane strain : $a, B \geqslant 2.5 \, (K_H / \sigma_y)^2$, where "a" is crack length and K_H is threshold stress intensity factor in hydrogen. Each specimen had a machined starter notch with a less

than 0.10 mm root radius, from which a fatigue precrack was extended so that "a" was at least equal to B (average "a" = 30 mm for WOL - IT). Two hard steel knives were also securely fastened at the front face of the specimen, for the measure of the crack opening displacement, V.

Test Environment

The hydrogen gas used was dehumidified and high-purity. Oxygen purification ($O_2 \leq 2$ wt-ppm) was obtained by passing the gas thru platinum powder. Dehumidification was performed using a cold trap. All specimens were also thoroughly cleaned in trichloro-ethylene, rinced in acetone and water, and dried. All tests were performed at room temperature.

Test Equipment

The equipment includes:a high pressure container that may accept up to 400 bars ; vacuum and pressurizing systems ; a loading equipment with an electronically controlled step by step motor ; two amplifiers and a chart recorder for crack opening displacement and load recording.
The container consists of a cylindrical part that is screwed to a round bottom through which a hole has been left for the loading rod, (torque shaft) as shown on fig.1. The cover of the container is made of two parts between which a rubber O-ring is pressed to ensure vacuum and high pressure sealing. All other seals, including loading rod seals, consist of rubber O-rings.
The specimen rests on a horizontal axle, so that loading is performed by pulling down the loading rod (fig.1). Before applying any load to the specimen however, the loading rod and surrounding pieces of equipment are pre-stressed, so as to prevent any stress relaxation while testing. Finally, the load is applied either continuously or step by step ; fatigue testing is possible using pre-programmed load variations.
Crack opening displacement is measured with a MTS clip-on gage ; load is measured using 16 strain gages fixed on a cylindrical piece of equipment that is placed below the specimen, and works in compression (see fig.1). Load and displacement strain gages, were periodically checked for eventual recalibration. All signals from the gages were amplified using Sedeme TS 105 amplifiers, and recorded.

K_H Measure

Once the specimen was screwed into place, a vacuum better than 10^{-5} bars was obtained, and hydrogen was flushed several times ; this allowed departure of possibly adsorbed impurities. Then the desired hydrogen pressure was set (up to 350 bars), and test was started once thermal equilibrium was reached. The method used here was one of constant crack opening displacement. A typical recording looks like the one on fig.2 : load is increased by small increments and left as such for a while ; if, at constant crack opening (that may be adjusted using the step by step motor), load does not vary, this corresponds to the crack not propagating. As soon as the crack propagates, the applied load decreases ; when it stops, one has reached the critical stress intensity factor in hydrogen, i.e. K_H. K_H is calculated using the compliance technique and recent values proposed by Saxema and Hudak (1978), as follows :
the compliance, $C = V_x/P$ at a distance x from the load line towards the front face, is given by :

$$C = \frac{BEV_x}{P} = \frac{BEV_o}{P}\left[\frac{X_o/W - X/W}{X_o/W + 0.2549}\right] \qquad (1)$$

where B is specimen thickness ; V_o = displacement at the front face ; E = Young's modulus ; P = load ; a = crack length ; W = width of the specimen ; X_o = distance from load line to the axis of rotation ; X = distance from load line to point where displacement is measured (this includes knives thickness).
Expressions for BEV_o/P and X_o/W are given by Saxema and Hudak (1978), for $0.2 < a/W < 0.975$, as :

$$\frac{BEV_o}{P} = \left[1 + \frac{0.2549}{a/W}\right]\left[\frac{1 + a/W}{1 - a/W}\right]^2\left[\sum_{i=o}^{8} b_i\,(a/W)^i\right] \qquad (2)$$

$$\frac{X_o}{W} = \sum_{j=o}^{5} c_j\,(a/W)^j \qquad (3)$$

where c_j's and b_i's are listed in Table 1 below.

TABLE 1. Coefficients b_i, c_j and d_k

i, j, k	0	1	2	3	4	5	6	7	8
b_i	4.3838	-37.588	359.68	-1319.5	2506.8	-2577.0	1203.5	0	-136.40
c_j	.408778	-1.52443	9.04028	-17.3354	15.9708	-5.56415	-	-	-
d_k	.8072	8.858	-30.23	41.088	-24.15	4.951	-	-	-

Thus, according to Eq.1, the compliance C, here measurable at any time since V_x and P are recorded, is a function of "a". Knowing C, one may then compute the crack length, "a", at any time.
But the stress intensity factor, K, is also a function of "a", for $0.2 \leq a/W \leq 1.0$, (Saxema - Hudak, 1978), according to :

$$\frac{K}{P}BW^{\frac{1}{2}} = \frac{2 + a/W}{(1 - a/W)^{\frac{3}{2}}}\left[\sum_{k=o}^{5} d_k\,(a/W)^k\right] \qquad (4)$$

where the d_k's are listed in Table 1.
Thus, a typical procedure for K_H measure is as follow : when the load stops from decreasing, as seen on fig.2, the compliance may be calculated from the measured values of V_x and P, and crack length "a" may be computed according to Eqs.1, 2 and 3. Knowing the value of "a" at crack arrest, one may then compute the value of K_H with Eq. 4.

Crack Growth Rate

At time t, on fig.2, the values of K and "a" may be calculated as K_1 and a_1, knowing P_1 and V_1 ; in the same way, at t_2, one has K_2 and a_2. Thus, for $K_m = (K_1 + K_2)/2$, the crack growth rate is given by $(a_2 - a_1)/(t_2 - t_1)$. Taking t_2 as close to t_1 as possible will give an even better estimate of the instantaneous crack growth rate. One will note that the technique does not prevent (da/dt) from being experimentally measured, as with a dc electrical potential technique (Johnson, 1966).

Fatigue Testing

Slow cycle fatigue tests were conducted with parameters $\Delta K = K_{max.} - K_{min.}$ in the

range 10 - 50 MPa $\sqrt{m}$, R = K_{min}/K_{max}, in the range 0.1 - 0.9, frequencies of the order of 0.05 - 0.25 Hz, and a sinusoidal wave contour.

MATERIALS

Chemical composition of this study's material is given in the table below :

TABLE 2. Materials chemical composition and σ_y's

Material	C	S	P	Si	Mn	Ni	Cr	Mo (wt %)
20 CN D10	.2	.015	.018	.235	.67	.85	2.76	.36
σ_y (MPa)	A : 900	B : 840	C : 700	D : 650				
A 533 Gr.B, Cl.1.	.185	.003	.010	.255	1.4	.665	.110	.510
σ_y (MPa)	E : 650	F : 600						
A 203, Gr.D	.105	.01	.01	.295	.625	3.52	.06	.01
σ_y (MPa)	G : 600	H : 550						

All materials were from industrial heats and quenched and tempered to get the desired stress level.

RESULTS

K_H Results

Values of K_H when it could be measured, are given in Table 3 ; when K_H was so high that plane strain conditions would not have been satisfied, the maximum value of K is given, and $K_H > K_{max}$:

TABLE 3. K_H Values at P_{H2} = 300 bars

Specimen :	A	B	C	D	E	F	G	H
K_H (MPa $\sqrt{m}$)	36	38	63	> 60	> 60	> 55	> 55	> 50
B (cm)	5	2.5	5	2.5	2.5	2.5	2.5	2.5
2.5 $(K_H/\sigma_y)^2$ (cm)	.4	.4	2	> 2.1	> 2.1	> 2.1	> 2.1	> 2.1

One will note that only three values of K_H at 300 bars could be calculated, and that they correspond to high yield strength materials. Fatigue precracks could not be propagated on other materials with lower σ_y values (σ_y < 650 MPa), without going over plane strain conditions ($B > 2.5 (K_H/\sigma_y)^2$) ; however, crack propagation was

obtained using fatigue testing, as seen later on.
The variation of K_H with hydrogen pressure is illustrated in fig.3 : K_H continuously decreases with P_{H2}. This result, and the particular shape of the obtained curves is in good agreement with literature data (M.J. Stowell et al, 1978).

Crack Growth Rate

Crack growth rate (da/dt) versus stress intensity factor is plotted on Fig.4. The results for alloy B' were obtained using another WOL - IT specimen that was heat treated similarly to alloy B (σ_y = 824 MPa) ; if one extrapolates the curve to low da/dt values, a K_H value of about 40 MPa $\sqrt{m}$ is obtained, i.e. a little higher than K_H for alloy B.

Fatigue Results

Fatigue results are plotted on Fig.5, for various ΔK, R and frequency values. One should notice that crack propagation was obtained for alloys (e.g. G and D) for which K_H could not have have been obtained without going over plane strain conditions. For instance, we had propagation, for alloy G, with K_H > 55 MPa $\sqrt{m}$, at ΔK = 41.5 and $K_{max.}$ = 53.5 MPa $\sqrt{m}$. Furthermore, crack propagation was found quite sensitive to $K_{max.}$; indeed, in the case of alloy B, at constant ΔK of 10.5 MPa $\sqrt{m}$, no propagation occurred at $K_{max.}$ = 36.5 MPa $\sqrt{m}$, while K_H = 38 MPa $\sqrt{m}$. Thus, although the critical threshold stress intensity factor in fatigue is lower than K_H, it is not far below it, in the ΔK, R and F ranges explored here.

DISCUSSION

The prime goal of this study was to test the possibilities of our technique, according to variables such as K, ΔK, R, F, P_{H2} and type of material. It is therefore interesting to compare our results with existing literature data.
Concerning K_H results, its evolution versus P_{H2} or σ_y is in agreement with predicted trends (Stowell and others, 1978) or with experimentally observed behaviours (Gerberich and Chen, 1975). Usually however, experiments are carried on steels with greater σ_y values (e.g., Gerberich and Chen, 1975, on 4340 steel with σ_y > 1000 MPa) ; thus it is not surprising that no K_H could be found on some of ours steels with σ_y < 650 MPa, as K_H increases rapidly with decreasing σ_y. Crack growth rates found in this study are also very much in the range commonly obtained (10^{-6} - 10^{-4} m/sec.) for similar steels and K values. As for the shape of crack growth rates curves versus K, we did not observe a stage II behaviour (plateau) as is sometimes found (e.g. Gangloff and Wei, 1977) ; this is probably due to the fact that, in our case, higher K values were not tried. However, it is worth noticing that the "plateau" of stage II propagation may only be present as a change in slope, as for AISI-4130 steel (Nelson and Williams, 1973) ; such a change in slope seems to be present here, particularly in the alloy B' case, Fig.4.
Similar remarks can be made concerning fatigue results, where values of da/dN obtained here are in the usual range for this type of material and test conditions (slow cycle fatigue : e.g. Stewart, 1977 ; Walter and Chandler, 1975). However, because all parameters were not systematically varied in this study, no formal conclusions can be drawn concerning the particular influence of each parameter.
One should finally point out some advantages of the technique : for one thing, a whole range of tests can be performed insitu on a given specimen, without having to take it out of the container ; also, loading is performed directly in hydrogen. Thus, possible contamination (e.g. O_2) of the crack tip is considerably decreased. Moreover, each K_H measure is made quite rapidly on a single specimen, without having

to use numerous specimens, such as for screw-loaded WOL - T. Concerning this last point however, K_H is considered as attained when the load does not decrease after at least a day exposure ; this could prevent very slow crack growth rates from being detected (e.g. 1µ/min.), and would give a slight overestimate of K_H. In order to answer that particular question, long duration tests have been started at our Laboratory ; first results after several hundred hours exposure at K values lower but close to K_H showed as yet no crack propagation. Thus K_H values seem quite correct, as also evidenced by the agreement with literature data.

CONCLUSIONS

The prime objective of this study was obtained : to develop a fast, reproducible and accurate technique that is able to give critical fracture mechanics data in hydrogen, such as K_H, da/dt or da/dN. Thus, various steel grades have been tested at different hydrogen pressures, that show distinct behaviours in agreement with literature data. More thorough studies on the individual effect of each parameter are now in process at Creusot-Loire.

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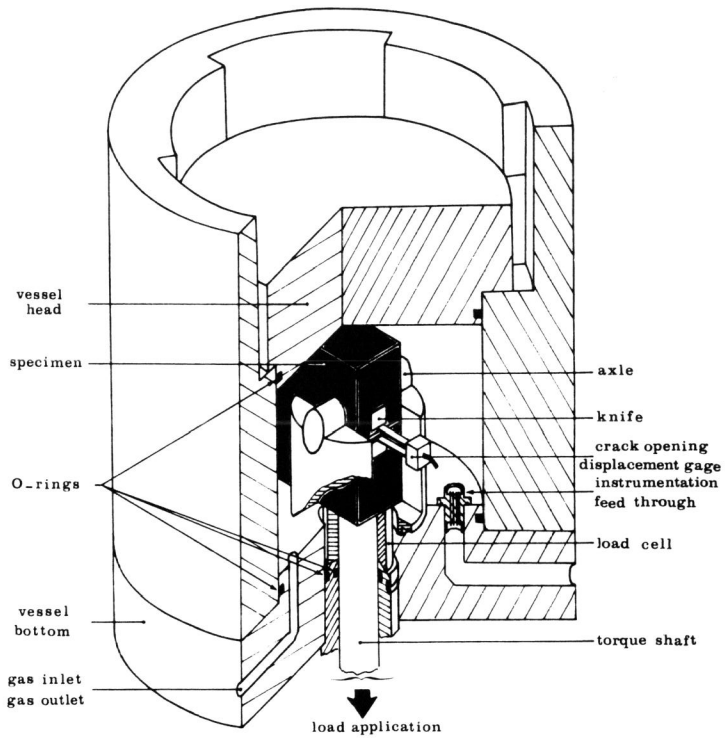

FIGURE 1 Test Equipment

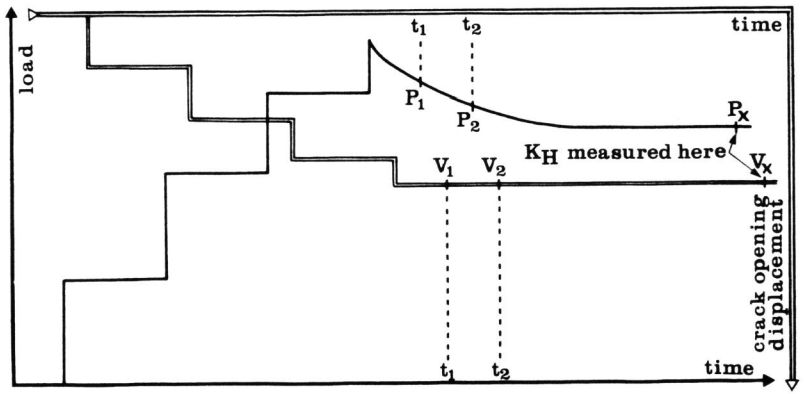

FIGURE 2 Example of test analysis

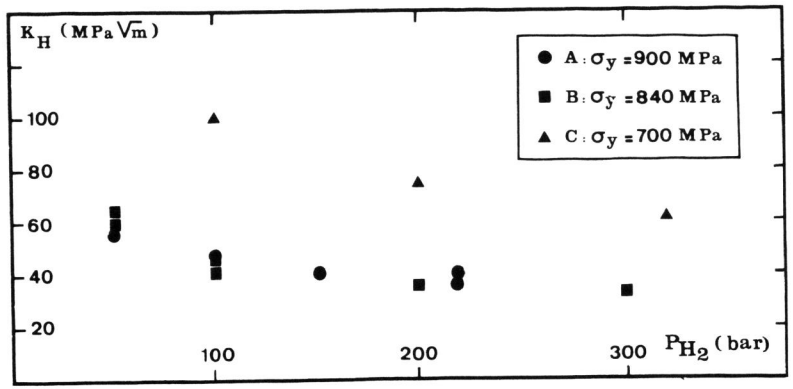

FIGURE 3

Variation of K_H with hydrogen pressure and material yield strength

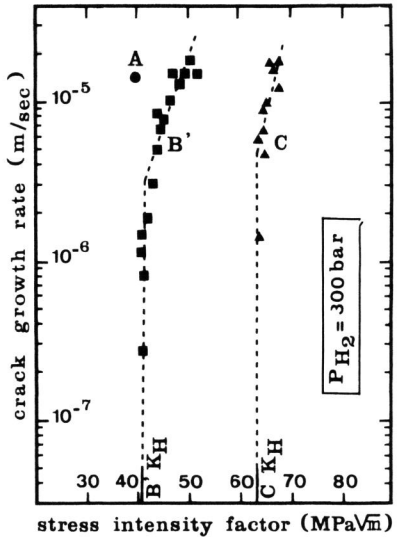

FIGURE 4

Crack growth rate versus K,
for alloys A, B' and C

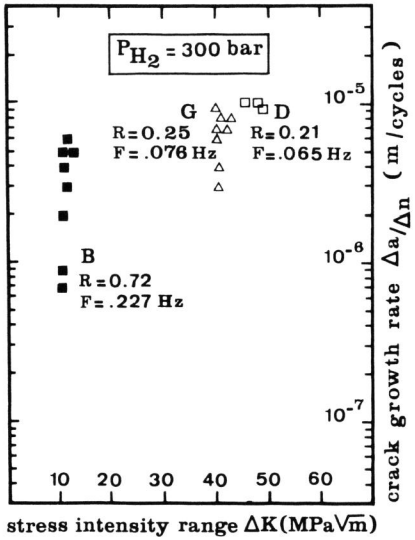

FIGURE 5

Fatigue crack growth rates
for various ΔK, R and F values