Influence Of Hydrogen Environment On Crack Growth Rate

L. Vergani[1], C. Colombo[1] and A. Sciuccati[1]

[1] Department of Mechanical Engineering, Politecnico di Milano, Via La Masa 1, 20156 Milano, Italy; Tel: +39 02 2399 8249; e-mail: laura.vergani@polimi.it

ABSTRACT. *Hydrogen as an energy carrier and hydrogen applications, as fuel cells, are considered to play an important role in energy storage. The study of the mechanical characteristic of steels under the influence of hydrogen embrittlement is an essential area due to the importance of these materials for mechanical system like fuel cells and huge infrastructure like pipeline and vessels. Metallic materials, such as carbon and low alloy steels, may suffer hydrogen damage and hydrogen embrittlement. A model to predict the hydrogen embrittlement crack growth rate in the II region of the da/dN-ΔK plot is suggested. This model will predict the behaviour of the material as a function of the experimental parameters such as: test temperature, load frequency and ΔK. In particular, once it is known the material behaviour without hydrogen and how hydrogen enhances embrittlement, it is possible to predict the crack growth rate and therefore the crack length after a certain number of cycles, at constant load, for a certain temperature and load frequency. This model rests on a superposition of effects: mechanical fatigue crack growth and purely hydrogen embrittled sustained growth.*

INTRODUCTION

In presence of H_2S and CO_2, metallic materials, such as carbon and low alloy steels, may be subjected to hydrogen damage and hydrogen embrittlement. The consequence of this phenomenon is a toughness reduction and an increase in crack growth rate, if there is fatigue.

In this paper, the attention is focussed on the mechanical fatigue behaviour of high-strength steels subjected to hydrogen embrittlement. These materials find their applications in pipelines and vessels, where they come in direct contact with sour environments. It is, therefore, important for these kinds of applications to have analytical models predicting crack growth rates and propagation.

In the literature there are several studies dealing with the influence of hydrogen on fatigue behaviour of carbon and low alloy steels, using the fracture mechanic approach, i.e., representing the data in terms of d*a*/dN - ΔK curves. These studies mainly aim to measure the fatigue properties of metals and welded joints in different environments, such as seawater, sweet (CO_2) or sour (H_2S) condensates, boiling or pressurized water in nuclear plants, gaseous hydrogen at high pressure [1-6].

The authors of [7-8] carried out several experimental studies on austenitic stainless steels, and evidenced the effect of hydrogen by considering the microscopic fatigue mechanisms, i.e. slip bands and striations. In [9] Murakami and Matsuoka showed the experimental results obtained by fatigue crack growth tests carried out on low−carbon, Cr−Mo and stainless steels. They considered the coupled effect of hydrogen content, hydrogen diffusion coefficient, load frequency, slip bands and strain−induced martensite in austenitic stainless steels.

In the present paper, fatigue experimental tests on C(T) specimens are carried out on two high-strenght steels in order to evaluate the crack growth rates in different environmental and loading conditions. An analytical model is developed, and data are fitted to check the validity of this model.

EXPERIMENTAL TESTS

Experimental tests are carried out on specimens obtained by two sections of seamless pipes in quenched and tempered conditions. The considered steels, widely used in chemical and petrochemical plants, are:

- 21/4Cr-1Mo steel, ASME SA-182 F22;
- micro-alloyed C-Mn steel, API 5L X65 grade.

C(T) specimens of F22 and X65 steels were cut from the pipes. The thickness of the specimens is B = 20 mm. The specimens have a C-L orientation, according ASTM E1823 and their dimensions and shapes are chosen accordingly to ASTM 647.

Specimens are tested both in "as received" conditions and with hydrogen charge, obtained by the electrochemical method described in details in [10].

The testing machine is a 100kN MTS 810 servo-hydraulic loading frame. All tests are carried out following ASTM E647–08 standard. Tests are carried out in load control, the cyclic load is applied as a sinusoidal wave with constant stress ratio R = 0.1. Measurements of crack growth are made through the compliance method. Before the test, the specimens are brought at the test temperature by immersion in an ethanol-liquid nitrogen bath. The fatigue tests are carried out by using a thermal chamber.

On both the steels, testing conditions are varied, considering three factors: the hydrogen absence or presence; the test frequency (f = 1 Hz; f = 10 Hz); the temperature (T = 23°C, T= -30°C). Details of the experimental tests can be found in [11].

From these tests, it was observed that F22 steel presents a linear trend of the crack growth rate da/dN, very well reproducible by the Paris law in inert condition (m = 3.2). Temperature have a limited influence on fatigue behaviour and frequency has no effect.

On the contrary, X65 steel in inert conditions has a double linear trend, but the Paris law can be used to interpolate the data, considering two formulations: a first one with higher slope (m = 4.4 for $\Delta K \leq 25$ MPa√m), and a second one with lower slope (m = 2.2 for $\Delta K > 25$ MPa√m). According to the literature, variations in Paris exponents can be attributed to microstructural properties and in particular to microstructure dimensions. This reduction of Paris exponent is found for aluminium and titanium alloys, but also for steels. It is related to a higher constrain to dislocation movements due to the microcrystalline structure[12].

For both the steels, hydrogen charged specimens showed a more scattered trend and an increase in crack growth rates. The crack growth rate curve is less dependent (lower *m* value) or even independent on ΔK, and the fatigue curves of hydrogen charged materials present a well–defined horizontal plateau.

ANALYTICAL MODEL

The considered model to describe crack propagation takes into consideration: test temperature, load frequency and ΔK. In particular, once it is known the material behaviour without hydrogen and how hydrogen enhances embrittlement, it is possible to predict the crack growth rate and therefore the crack length after a certain number of cycles, at constant load, for a certain temperature and load frequency.
In the literature, the fatigue behaviour of metals in aggressive environments, is simulated by a superposition model [13]. Its formulation is:

$$\left(\frac{da}{dN}\right)_{TOT} = \left(\frac{da}{dN}\right)_{B} + \int_T \frac{da}{dt}\left[K(t)\right]dt \tag{1}$$

where the suffix B stands for baseline fatigue (mechanical fatigue of the inert metal, estimated by the Paris law) and the integral in Eq.1 is taken over one cycle of the fatigue loading, representing the “environmental cracking”. It incorporates the effect of frequency, *f*, and stress ratio, *R*, via the dependence of the crack length *a* on the stress intensity factor K(t). The graphical representation of this model is shown in Fig. 1.
Considering the dependency of the crack propagation on temperature and frequency,
Eq. 1 can be simplified as:

$$\int_T \frac{da}{dt}\left[K(t)\right]dt \cong \frac{d\overline{a}}{dt}\int_T dt = \frac{d\overline{a}}{dt}t = \left(\frac{d\overline{a}}{dt}\right)_{IHAC}\frac{1}{f} \quad with \quad \int_T \frac{da}{dt}\left[K(t)\right] \cong \left(\frac{d\overline{a}}{dt}\right)_{IHAC} \tag{2}$$

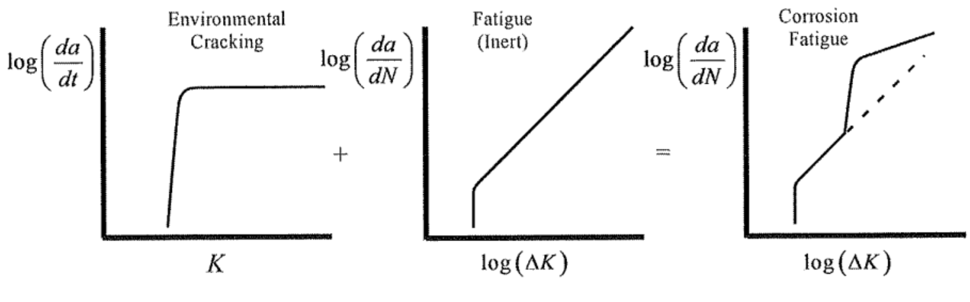

Figure 1. Schematisation of the superposition model [13].

where $\left(d\bar{a}/dt\right)_{IHAC}$ is the average sustained load fracture rate owing to internal hydrogen assisted cracking (IHAC) and, since the integral in Eq. 1(was calculated over one loading cycle, $t=1/f$. Therefore, the superposition model, given in Eq. 1, can then be rearranged as it follows:

$$\left(\frac{da}{dN}\right)_{TOT}=\left(\frac{da}{dN}\right)_{B}+\frac{1}{f}\cdot\left(\frac{d\bar{a}}{dt}\right)_{IHAC} \tag{3}$$

Hence, the superposition of both crack growth rates (i.e. baseline and IHAC) should give the frequency dependence of the overall crack propagation rate (TOT) once the behaviour in the Region II of the uncharged material and the average sustained load fracture rate $\left(d\bar{a}/dt\right)_{IHAC}$ are known.
For both the tested steels, it is firtly evaluated the coeffient of the Paris law:

F22 steel:	$C = 2.3\cdot10^{-9}$ *mm/cycle*	$m = 3.19$		
X65 steel:	$C_I = 1.01\cdot10^{-10}$ *mm/cycle*	$m_I = 4.37$	for $\Delta K<25.5 MPa\sqrt{m}$	(4)
	$C_{II} = 1.04\cdot10^{-7}$ *mm/cycle*	$m_{II} = 2.22$	for $\Delta K>25.5 MPa\sqrt{m}$	

Then, the average crack growth rate per cycle due to the hydrogen embrittlement is estimated by taking as reference either T = 23 °C and *f* = 1 Hz or the average of crack rates at different frequencies, using the following relation, obtained from Eq. 3:

$$\left(\frac{d\bar{a}}{dt}\right)_{IHAC}=\left(\left(\frac{da}{dN}\right)_{TOT}-\left(\frac{da}{dN}\right)_{B}\right)\cdot f \tag{5}$$

Analytically, the average crack growth rate per cycle owning to the hydrogen embrittlement was found according to Eq. 5, by subtracting the data of the uncharged steel $\left(da/dN\right)_{B}$, that is Paris relation, from $\left(da/dN\right)_{TOT}$ of the charged specimen at the same ΔK in a range where still the IHAC effect is predominant (plateau region). When crack propagation rate is much higher than the uncharged material, the estimation can be performed by dividing the crack growth per cycle by the cycle period (T=1/f) in the plateau region. The reason why only this region is considered is that in the plateau the hydrogen embrittlement contribution to crack growth is almost 2 orders of magnitude compared to the uncharged case.
Another parameter that should be estimated to improve the model approximation is ΔK_{start}, that is the ΔK value where crack propagation begins to be influenced by the presence of hydrogen and crack growth rate increases:

$$\left(\Delta K\right)_{start}=K_{start}\cdot\left(1-R\right) \tag{6}$$

where R is the stress ratio. From experimental results it was noticed that ΔK_{start} is in the range of 12.5÷14.5 MPa√m.

It can be assumed that the upper boundary of the model reaches asymptotically the critical K value of the material. Since the model predicts a superposition of effect, a transient is observed where hydrogen assisted cracking approaches the $\left(d\bar{a}/dt\right)_{IHAC}$ rate in a range of ΔK from the threshold to the plateau. In order to avoid a step in correspondence of ΔK_{start} and provide for a continuous crack growth rate, it was choosen to gradually introduce the effect of hydrogen embrittlement. An interval of 2 MPa√m was selected to gradually introduce $\left(d\bar{a}/dt\right)_{IHAC}$ contribution, as it follows:

$$\left(\frac{da}{dN}\right)_{TOT} = \left(\frac{da}{dN}\right)_{B} + \frac{1}{f}\left(\frac{d\bar{a}}{dt}\right)_{IHAC} g(\Delta K) \tag{7}$$

where the function g(ΔK) is defined as:

- $g(\Delta K) = 0$ if $\Delta K < \Delta K_{start}$;
- g(ΔK) is a function of ΔK ranging from 0 to 1 when $\Delta K_{start} \leq (\Delta K) \leq \Delta K_{start} + 2$;
- $g(\Delta K) = 1$ if $\Delta K > \Delta K_{start} + 2$;

Finally, the variation in crack growth rate at different test temperatures can be compared to the variation of the diffusion coefficient D from T = 23 °C to T = −30 °C [11]. In steels, the dependence of D on temperature is rather well predicted by the following relation [14]:

$$D = D_0 \cdot e^{\frac{-E_a}{RT}} \quad \left[m^2/s\right] \tag{8}$$

where:

- D_0 is a pre-exponential factor;
- E_a is hte activation energy;
- R is the gas constant, equal to 8.31 [*J/mol*];
- T is the temperature [*K*].

It was found that crack growth rate and diffusion coefficients ratios at different temperatures are very similar [11]. Therefore, the variation of diffusion coefficient, due to the temperature change is the main parameter responsible of the change in crack growth rate. Since the ratio between diffusion coefficients cancels the influence of D_0, the only parameter that should be calculated is the activation energy for diffusion E_a, that can vary largely in the process zone owing to presence of high energy hydrogen traps such as dislocations, vacancies and the stress state itself, whose concentration is different than in the bulk material [15]. Activation energy for X65 and F22 steels is taken from literature equal to 15.5 kJ/mol, nevertheless this value can vary largely and depends on the site where the hydrogen is: low energy, when interstitial (E_a = 1.6 kJ/mol) and high energy, when trapped (E_a = 60 kJ/mol).

APPLICATION OF THE MODEL TO THE EXPERIMENTAL DATA

Tab. 1 shows a summary of the analytical crack growth rates for the two considered steels in internal hydrogen assisted cracking conditions (IHAC). Combining these values and Eq. 7, the trend of the crack growth rates is then evaluated for the other considered frequencies.

Figs.2-5 show the comparison between the analytical model and the experimental data for the two considered steels and for room temperature and T = -30°C. It can be noted a good approximation between almost all the test data and the model estimations.

The superposition model seems to fit reasonably the test data with respect to all the dependences on environmental conditions and material behaviour, and it agrees with previous investigations found in bibliography. It appeared that test data at low frequency and room temperature are better focused on the expected value and for this reason they should be used for the interpolation. The lack of the knowledge of ΔK_{th} can be a limit when short cracks are considered (short crack mechanic needs a different approach), nevertheless the model is a powerful and relatively simple tool in order to evaluate crack growth rates at different conditions without a large number of tests.

Table 1: Summary of the analytical crack growth rates in internal hydrogen assisted cracking conditions (unit: mm/s).

Material	$\left(\frac{d\bar{a}}{dt}\right)_{IHAC}^{T=23°C,f=1Hz}$	$\left(\frac{d\bar{a}}{dt}\right)_{IHAC}^{T=-30°C,f=1Hz}$
F22	$2.48\cdot10^{-3}$	$6.28\cdot10^{-4}$
X65	$2.23\cdot10^{-3}$	$5.65\cdot10^{-4}$

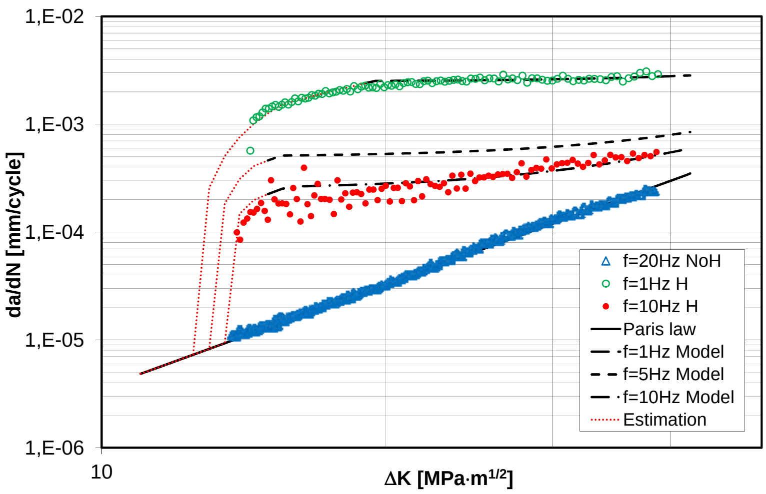

Figure 2: F22 steel: model prediction and experimental data at T = 23 °C.

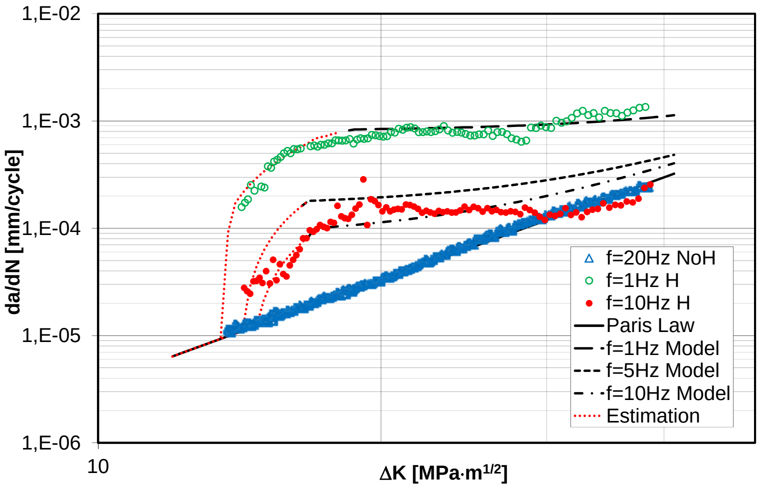

Figure 3: F22 steel: model prediction and experimental data at T = –30 °C.

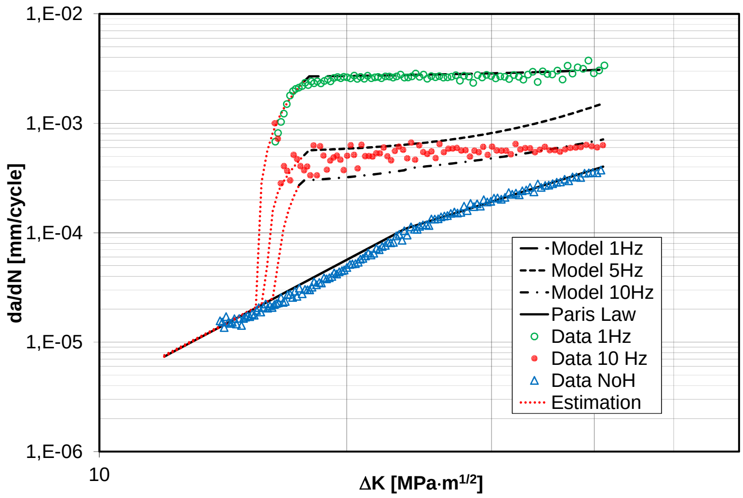

Figure 4: X65 steel: model prediction and experimental data at T = 23 °C.

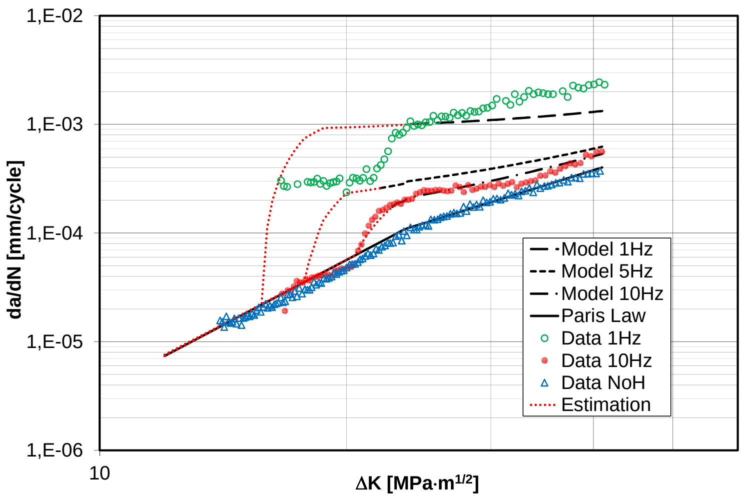

Figure 5: X65 steel: model prediction and experimental data at T = –30 °C.

CONCLUSIONS

The effect of hydrogen on the fatigue crack growth rate of two steels, widely used in oil pipelines, has been investigated varying test frequency and temperature. In conclusion:

- an analytical model is proposed, taking into consideration frequency and test temperature; this model is able to predict the fatigue behaviour of steels in presence of hydrogen;
- the analytical model is based on a superposition effect; crack growth rate, in hydrogen charged material, is the sum of two contributions: one named "mechanical", that depends on applied loads, and a second one due to hydrogen effect. When crack growth rate increases, the "mechanical" contribution prevails because hydrogen atoms do not have enough time to accumulate at the crack tip: as a consequence crack growth rate is no longer hydrogen dependent;
- the model gives good results and fits satisfactorily the experimental data.

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