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Fatigue behavior of hydrogen pre-charged low alloy Cr–Mo steel

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ABSTRACT

Aim of the present work is to study the mechanical behavior in presence of hydrogen of a quenched&tempered low alloy Cr–Mo steel, AISI 4130, used for hydrogen storage and transportation. The sensitivity of steels to hydrogen embrittlement is generally determined by means of two kinds of experimental procedures to hydrogen charge the specimens: gaseous hydrogen in environmental chambers or autoclaves or H_2S solution (recommended by NACE standard). In this work experimental tests are carried out on specimens pre-charged by means of an electrochemical method. A campaign of toughness and fatigue crack growth tests is performed on specimens without and with pre-charged hydrogen. The results are compared and discussed with other, from literature, obtained by following more traditional testing procedures.

By this comparison the adopted experimental procedure, that is safer and easier, seems to provide useful information.

1. Introduction

At present time the increasing energy demand has driven, on the one hand, the development of new oil and gas fields around the world, many of which are sour and, on the other hand, the research of new, sustainable energy sources, as fuel-cell technology, and the use of hydrogen as energy carrier.

These cases involve the utilization of pipelines and huge infrastructures for the transportation of hydrogen or of sour oil and/or hydrocarbon, both dealing with the problem of hydrogen embrittlement.

Up now, this topic is widely debated in literature. Many efforts are made by researchers in order to enhance and deepen the knowledge of this phenomenon through both experimental studies and modelling at different scale [1–8].

However, the new applications in energy fields require challenging issues for higher operative performances in aggressive working environments, to avoid catastrophic consequences for environment, industrial economy and personnel health. Besides, a full knowledge of the mechanical behavior of metallic materials directly in contact with hydrogen, and in particular a quantification of the hydrogen influence on mechanical properties of steels, is certainly a need for a proper design of these components and structures, as well as to ensure a correct maintenance.

In order to design performing components during their service life up to several years, it is essential to have a reliable database of experimental tests under repeatable testing conditions, referred to the particular environmental conditions where the structure is supposed to work. In literature, such a database is still lacking, due to the complexity of the testing procedure that should simulate the environmental conditions, in which embrittlement happens.

Examples of dangerous environmental conditions are related to the presence of gaseous hydrogen (infrastructure for the storage and transportation of hydrogen) and of acid and sulfide in oil and hydrocarbon, when hydrogen atoms originated from the cathodic reduction reaction can diffuse into the steel (pipelines to export hydrocarbon from sour oil&gas fields).

The experimental procedure should reproduce these conditions to induce the formation of atomic hydrogen on the steel surface. In literature, two different experimental procedures are present: (1) the *in situ* procedure with gaseous hydrogen, (2) the *in situ* procedure with H_2S.

The first procedure uses low (0.1–0.2 MPa, [9–11]) or high pressure (up to 100 MPa, [12]) gaseous hydrogen in environmental chambers or autoclaves. Firstly, vacuum is created to ensure that the total concentration of background gases, as O_2, H_2O, N_2, would be lower than the concentration of hydrogen. Secondly, the test chamber is filled up with hydrogen, the contaminant gas, and afterwards experimental tests can be performed. Testing equipment is placed inside the chamber: in this way, both static and

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Nomenclature

a	crack length
C, m	coefficients as in Eq. (1)
E	Young modulus
f	testing frequency
J_{IC}	J toughness without hydrogen
J_H	J toughness with hydrogen
K	stress intensity factor
K_{JIC}	K toughness without hydrogen, evaluated from J_{IC}
K_{JH}	K toughness with hydrogen, evaluated from J_H
K_H	K toughness with hydrogen
N	number of cycles
σ_y	yield strength
σ_{UTS}	ultimate tensile strength

cyclic loads can be applied to the specimens. Although this procedure ensures a constant hydrogen flow from the specimen surface to its core during the test, and any loading condition (static and cyclic), it requires a source of purified hydrogen and highly controlled testing conditions to be continuously monitored and recorded.

The second procedure is obtained by means of hydrogen sulfide, H_2S in aqueous solutions, and it is recommended in NACE standard TM 0177 [13]. This standard aims giving indications and specification for the optimum selection of materials having minimum susceptibility to *sulfide stress cracking* (SSC) in H_2S environments [14]. Loads are applied during environmental testing: constant load, constant deformation and slow strain rate tests can be performed according to [13]. Particular attention must be paid, since H_2S is highly toxic and not safe, and must be handled with care.

These procedures to hydrogen charge specimens are complex, dangerous and expensive, besides it is difficult to carry out experimental tests as toughness and fatigue crack propagation, unless building *ad hoc* loading frames (*e.g.* [15]).

In this work another experimental procedure has been followed: the electrochemical pre-charge method. By this technique, specimens are hydrogen charged before testing by an electrochemical procedure. Generally, specimens are used as cathodes in a solution, typically acidic, with a defined galvanostatic current density. Newman and Shreir [16] are the authors of one of the first paper dealing with the electrochemical hydrogen charging. A state of the art about hydrogen electrochemical charging is reported in [17].

This pre-charging electrochemical procedure is, of course, safer (no high pressure of gaseous hydrogen or H_2S is required) and less expensive than the other ones. It allows a more convenient experimental set up; in fact, after hydrogen pre-charge the specimens can be tested by using traditional testing equipment.

On the other side, in this type of tests mechanical loading is carried out on hydrogen pre-charged specimens while in NACE stress corrosion crack (SCC) and corrosion fatigue (CF) tests the environmental effect is present at the same time of mechanical loading. In this way, hydrogen is continuously supplied on the metal surface. It is therefore very important to verify that the effects of the different experimental procedures are comparable and with this aim, a literature survey is performed.

Williams and Nelson [18] focuses the attention on toughness and fatigue tests, proposing a comparison between the results of experimental tests obtained charging some specimens by low pressure *in situ* gaseous hydrogen system and some other by electrochemical pre-charging method. All specimens are made from AISI 4130 steel. The authors concluded that the two different experimental procedures cause the same embrittlement phenomenon. They found out these conclusions by analyzing both the experimental results (in terms of toughness and fatigue crack growth rate values) and the fracture surfaces. Similar conclusions were confirmed also in a recent work [12], in which fracture surfaces of three different kinds of charging: (1) specimens tested in air; (2) electrochemically hydrogen pre-charged specimens; (3) high-pressure H_2 gas charged specimens are examined.

The material considered in this work is a low alloy Cr–Mo steel, namely AISI 4130. Fatigue crack growth and toughness tests are performed by considering hydrogen pre-charged and hydrogen-free specimens.

Obtained experimental results are compared with other data from literature achieved with the same material and tested in gaseous hydrogen [18,19]. These authors carried out toughness and fatigue crack growth tests and evidenced the effect of gaseous hydrogen pressure on material mechanical behavior and embrittlement phenomena.

On the contrary, [20] performed experimental tests on AISI 4130 steel, by hydrogen charging the specimens in H_2S aqueous solution.

The results of all these experimental campaigns are compared, with the aim to verify the effectiveness of the pre-charging procedure and even to quantitatively compare the experimental obtained values with equivalent ones from literature.

2. Material

Object of this study is a low alloy Cr–Mo steel (AISI 4130), quenched&tempered, with a tempered martensitic microstructure. Table 1 reports the mechanical properties, obtained from experimental tensile tests, and the chemical compositions.

Table 1
Mechanical properties and chemical composition (%) of AISI 4130 steel.

σ_y (MPa)	σ_{UTS} (MPa)	E (MPa)	C	Mn	Si	Cr	Mo
715	950	220,000	0.30	0.50	0.25	0.95	0.20

3. Experimental equipment and setup

The testing procedure is as follows:

- sample machining;
- fatigue pre-cracking. All samples are pre-cracked in air up to approximately a crack length $a = 2.6$ mm;
- hydrogen pre-charging;
- fatigue crack growth or toughness test. All the tests are performed by means of a servo-hydraulic testing machine, MTS Landmark, equipped with a load cell of 100 kN capacity. Clip on gage is applied during the tests to measure the crack opening displacements. Measure of crack length is performed by means of the compliance method.

In the present work, specimens are hydrogen pre-charged by an electrochemical technique, adapted from the literature and set up at the Politecnico di Milano. Specimens are cathodically polarized by a constant current density of 0.5 mA cm^{-2}. The solution,