Hydrogen effects on low cycle fatigue of high strength steels

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Hydrogen absorption occurs during steelmaking processes and causes detriment on mechanical properties, such as plasticity, fatigue strength and tensile strength, among others. The main purpose of the present paper is to study the hydrogen effects on the low cycle fatigue behaviour of a high strength steel, resulphurised and microalloyed. Before the cyclic tests, samples are cathodically charged using a H_2SO_4 acid solution. In some samples, poisons are added. The flow stress evolution during cycling was studied by analysing the so called 'back' and 'friction' stresses derived from the hysteresis loops. Fatigued specimens were observed through scanning electron microscopy and transmission electron microscopy. Additionally, the metallographic technique known as 'silver decoration' allows evaluation of the hydrogen distribution in the structure by applying energy dispersive analysis. The higher stress levels and cyclic softening rates exhibited by hydrogen charged samples in comparison with uncharged ones are related with the friction stress behaviour. The hydrogen is found mainly associated with MnS inclusions.

Keywords: Steel, Hydrogen embrittlement, Fatigue, Poisons

Introduction

During steelmaking processes, structural steels are exposed to hydrogen contaminated environments and suffer premature fractures in service. Thus, hydrogen embrittlement has had a relevant scientific research interest.[1–4] Nevertheless, up to now, hydrogen effects on mechanical properties are not completely understood. It is well known that when hydrogen is trapped in microstructural defects, such as vacancies, dislocations and MnS inclusions, it may affect the mechanical behaviour of the materials.[5–8] Even though the hydrogen effects on the monotonic response of steels have been studied intensively, little information is available on the cyclic stress response.[9,10]

Uyama *et al.*[11] reported that no significant differences in fatigue life between hydrogen charged and uncharged specimens were observed in a steel (0·47%C) tested under constant stress amplitude. However, the total strain amplitude of the hydrogen uncharged samples increased more rapidly than the hydrogen charged ones. Moreover, the saturation value of the hydrogen charged specimens was lower than that of the hydrogen uncharged specimens. Thus, hydrogen uncharged samples showed a more pronounced cyclic softening.

According to Han and Feng,[12] the initial stress amplitudes of the hydrogen charged samples of 2·25Cr–1Mo steel are higher in comparison with the uncharged ones. In addition, an increase in cyclic softening rate and a decrease in the fatigue life take place due to hydrogen. The increase in cyclic softening rate in hydrogen charged specimens was ascribed to the enhancement of microvoid initiation and the growth produced by hydrogen from secondary phase particles. Additionally, these researchers stated that the decrease of the drag effect of hydrogen atoms on moving dislocations is also useful for increasing the cyclic softening rate.

Hereñú *et al.*[13] reported cyclic softening effects due to hydrogen in high strength steel. This fatigue response was explained by the dislocation transport of hydrogen towards non-metallic inclusions being much faster than in conventional lattice diffusion.

On the other hand, Tsuchida *et al.*[14] discussed possible mechanisms for fatigue property degradation by hydrogen. They performed a low cycle fatigue test, at different strain rates, in low carbon steel that contains small amounts of pearlite. Their main results are expressed as follows:

(i) most of the hydrogen is dissolved in the lattice, and the rest is trapped by pearlite
(ii) a decrease in fatigue life associated with an increase of stress amplitude is observed due to hydrogen
(iii) hydrogen gasified at the interface between matrix and non-metallic inclusion, promoting both initiation and propagation of fractures with a circular surface 'fish eye'.

The entrapment of hydrogen in iron and steel is undesirable because of the degradation caused on the mechanical properties. Nevertheless, during the final processing of the steel products (galvanising, electrodeposition, etc.), the

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entrapment cannot be avoided. In such a situation, the different species present in the environment act as promoters, increasing the kinetics of hydrogen entry in the metal. Conway *et al.*[15] examined the effects of coadsorbed S and As in samples that contain catalyst poisons. They observed the evolution of cathodic kinetics and H absorption on Pt, Pd and Fe and concluded that the H transfer rates through Fe membrane are increased by the presence of As in the charging solution. Other researchers[16,17] studied As compound influence on hydrogen entry into steels. They suggested that, initially, the AsO_2 absorbed by metals at high cathodic over potentials is reduced to metallic As^0 and finally transformed into AsH_3 gas.

Using the method proposed by Kuhlmann-Wilsdorf and Laird (Fig. 1),[18] the physical mechanisms responsible for hardening or softening can be identified from the hysteresis loop shape. This method assumes that the flow stress needed to produce plastic deformation during cyclic tests is composed of two contributions. One is a thermal component, named friction stress, caused by short range obstacles, foreign atoms and lattice friction, to dislocation slip. The other component, called back stress, is almost temperature independent and originated from long range barriers, as dislocation configurations, precipitates and grain boundaries, too high to be overcome with thermal activation contribution. The applied stress is the sum of the friction stress σ_F and the back stress σ_B. Information on the types of obstacles to dislocation movement can be obtained from the measurement of these stresses.

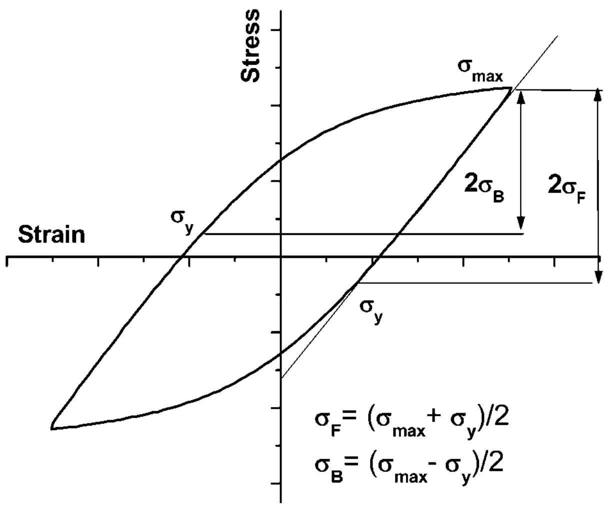
Thus, the purpose of the present paper is to analyse the influence of hydrogen precharged samples on the fatigue behaviour of high strength steel. Moreover, in some cases, promoters such as As_2O_3 were added to the electrolytic solution in order to evaluate the effect on the H absorption kinetic.

Experimental

Cylindrical bars of structural and forged resulphurised high strength steel were used for this study. The chemical composition of steel is presented in Table 1. A metallographic study was carried out using an Olympus GX51 light microscope with an image analyser system Leco IA 32. The microstructure consists of pearlite grains with ferrite at the grain boundaries. In addition, incipient pearlite spheroidisation is found in some grains. The grain size measured is ~30 μm.

Cylindrical fatigue samples with a gage length of 18·4 mm and a diameter of 5 mm were machined from the bars. The longitudinal axis of the samples was parallel to the bar rolling direction; this option minimised the effect of manganese sulphide stringers present in the material that could affect crack propagation.

Before mechanical tests, hydrogen cathodic charge was performed at room temperature. The charging procedure was developed by employing a direct current density of 36 mA cm^{-2} for 1·5 and 6·5 h in a solution of 1 N H_2SO_4 with graphite electrode. In some cases, the addition of hydrogen promoters such as As_2O_3 diminishes the pH up to 1·26. Once charged, the specimens were carefully cleaned, dried and put into sealed recipients until the mechanical tests were carried out. Taking into account that the present paper analyses the influence of trapped hydrogen on the cyclic behaviour, the time elapsed between charging and testing produces minor effects.



1 Schematic representation of friction and back stresses

Cyclic deformation tests were carried out in air at 20°C in an Instron 1362 testing machine under total strain control with total strain ranges of 0·85 and 1·5%. A fully reversed triangular form signal of 10 s period was selected. The analysis of the internal and effective stresses during cyclic loading was made using a computer program applied to the data recorded directly from the test machine. The measurement accuracy is ~5%.

A special metallographic technique, named as microprint, developed by Schober and Dieker,[19] was employed to reveal the hydrogen presence and distribution in the structure by applying an Ag solution salt. Because of the hydrogen interaction with salt, metallic Ag particles are reduced. When metallographic samples are observed with scanning electronic microscopy (SEM), those bright irregular particles of Ag reveal where hydrogen is occluded.

After fatigue tests, the fracture surfaces were analysed by SEM while dislocation structures were observed by transmission electron microscopy.

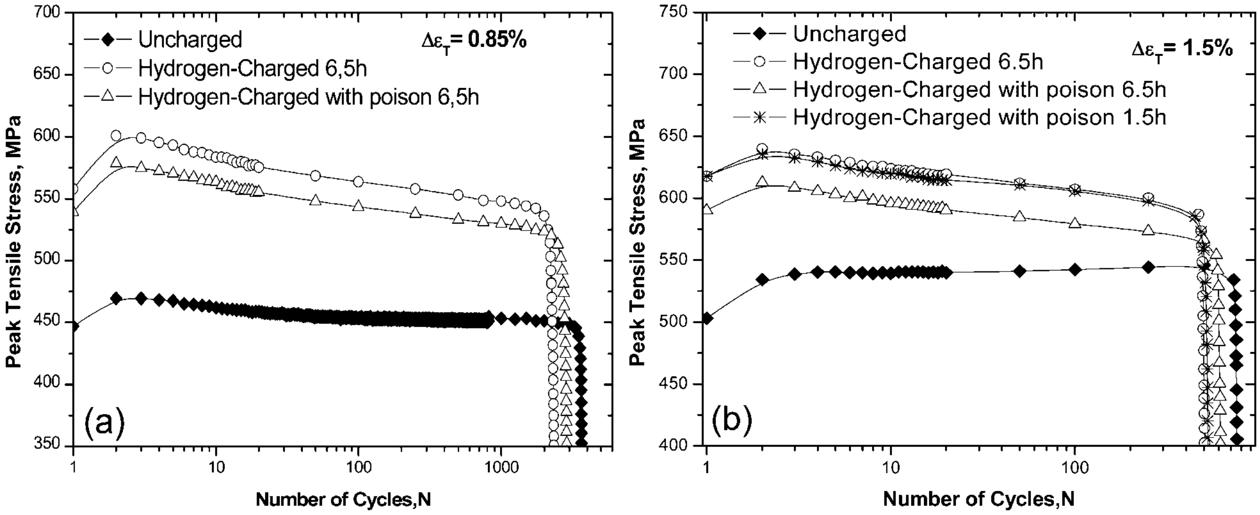
Results and discussion

Figure 2 shows the cyclic behaviour of hydrogen charged and uncharged samples at total strain ranges of 0·85 and 1·5%.

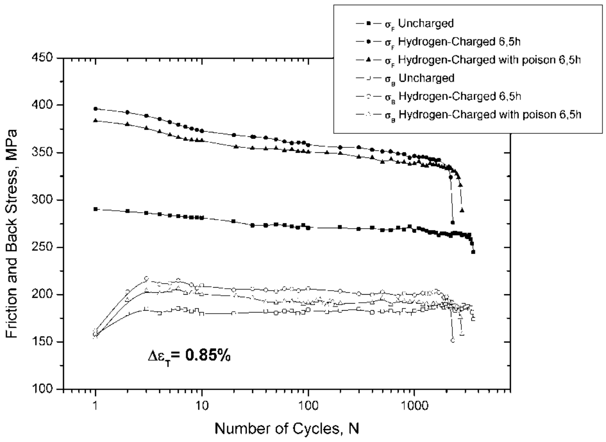
For both strain ranges, all the samples (charged and uncharged with hydrogen) initially exhibit a short cyclic hardening period. Then, the hydrogen charged samples cyclic soften up to rupture, whereas the uncharged samples attain a saturation stage. Moreover, independent of the charging conditions, the softening rate seems to be the same. It is important to remark that in hydrogen charged samples there is a strong increase of stress level in comparison to uncharged ones.

Table 1 Chemical composition in wt-%

C	0·41	V	0·01	P	0·02
Mn	1·82	W	<0·045	S	>0·088
Ni	0·06	Ti	0·17	Si	0·15
Mo	0·058	Sn	0·014	Cu	0·17
Nb	<0·045	As	0·01	Cr	0·16



2 Cyclic response of high strength steel



3 Friction and back stress of hydrogen uncharged and charged samples

Furthermore, poison addition plays the same role as increasing the charging time (Fig. 2*b*). The stress increment due to hydrogen decreases with poison additions and at higher strain range. Fatigue life is reduced in charged samples in comparison with uncharged ones.

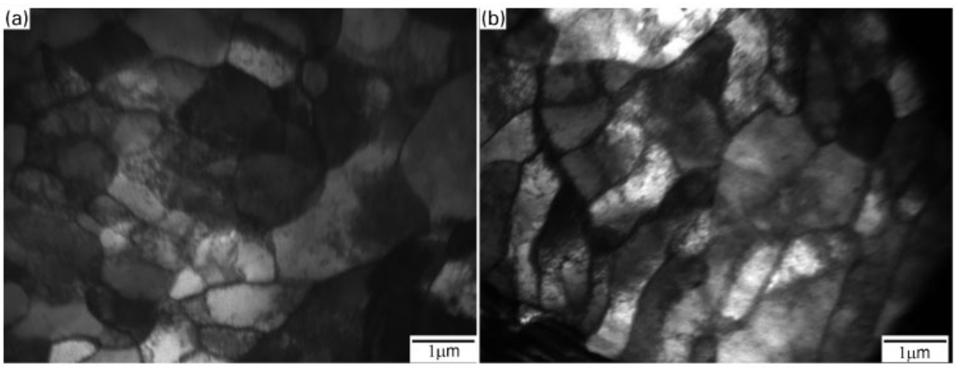
Figure 3 shows the evolution of friction stress σ_F and back stress σ_B in uncharged and charged samples. It is important to remark that for charged samples σ_F attains higher levels than uncharged specimens. This increase in σ_F levels could be explained through dislocation pinning by hydrogen. During cycling, the dislocations seem to unlock from their pinning points, leading to a decrease in σ_F for the next cycle.

As regards the analysis of σ_B, no remarkable changes are found between uncharged and charged samples in most of the fatigue life. At failure, dislocation cells are the characteristic cyclic structure usually found in ferrite despite charging conditions and strain range imposed (Fig. 4). Thus, the increase of mobile dislocations as cycling proceeds in charged samples seems not to interfere with the final fatigue dislocation arrangement. It can be presumed from these results that the cyclic hardening–softening differences between charged and uncharged samples are mainly determined by the friction stress component.

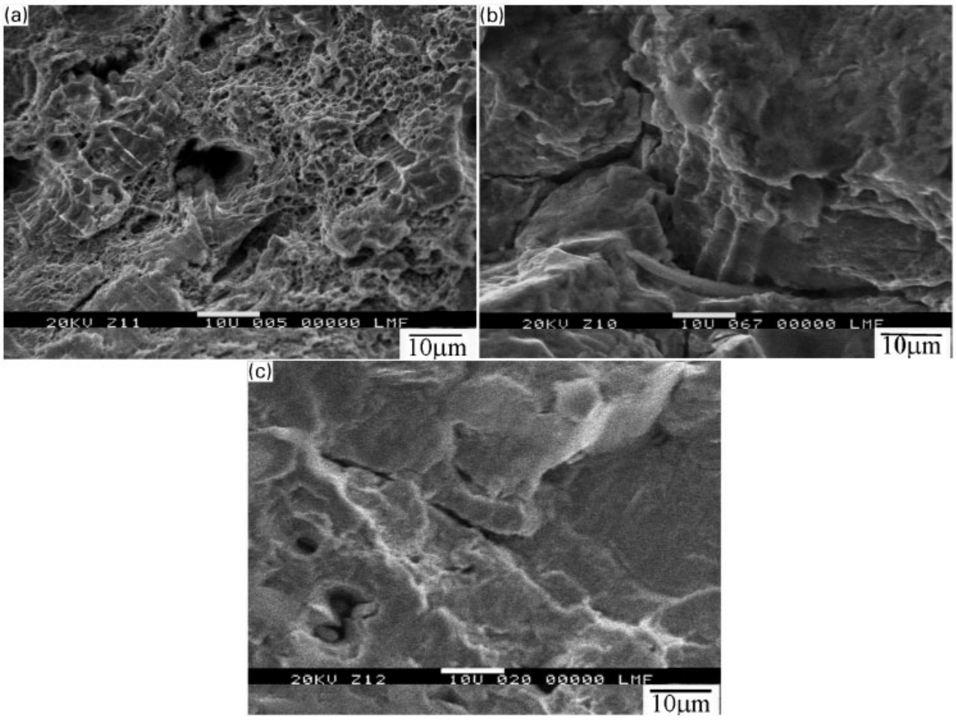
The fracture surface of uncharged specimens shows a typical ductile mode by microvoid coalescence mechanism and fine dimples representing marked plastic surface (Fig. 5*a*).

Nevertheless, hydrogen charged samples develop a mixed fracture surface, showing a predominant 'quasi-cleavage' aspect. However, signs of ductile behaviour like river pattern and small dimples are visualised (Fig. 5*b* and *c*).

In hydrogen charged samples, cracks coalescence around the MnS are found. It should be noted the hydrogen assisted crack area decohesion of the inclusion from the matrix. Hydrogen presence, revealed by means of fine Ag° particles, is evidenced around the MnS particles (Fig. 6). Thus, because of the synergistic effect



4 Dislocation structure in *a* uncharged and *b* hydrogen charged samples

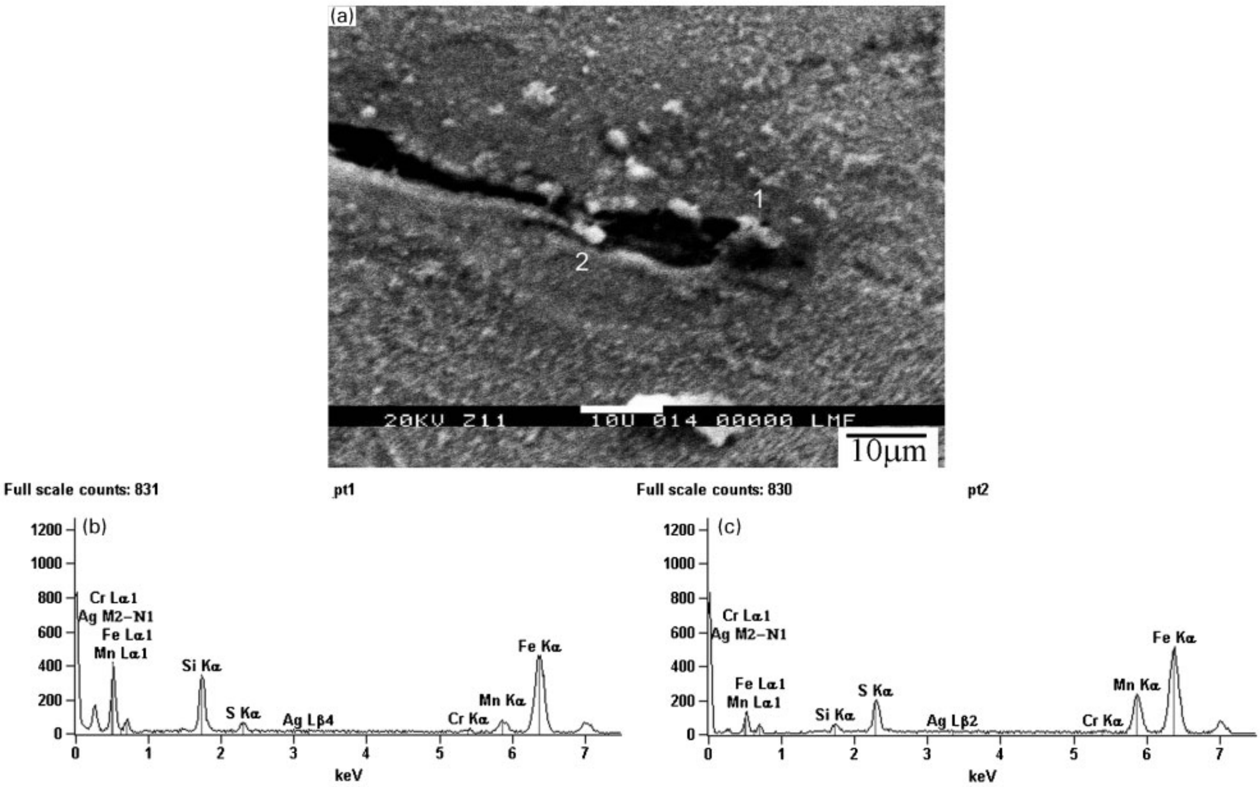


a uncharged sample; *b* hydrogen charged sample at 6·5 h; *c* hydrogen charged sample with poison 6·5 h

5 Fracture surface zones at total strain range of 1·5%

of hydrogen and the non-metallic inclusions, hydrogen is trapped in these sites.

Several authors[12,13,20] reported that through dislocation movement, hydrogen is released in the vicinity of inclusions, enhancing crack nucleation and growth, which lead to the observed cyclic softening and quasi-cleavage fracture surface. The results of the present paper reveal that dislocation structure evolution has no appreciable influence on the cyclic softening of high strength steel. This fact is in agreement with the



a metallic Ag particles surrounding matrix decohesioned sulphide; *b* energy dispersive analysis of particles marked as 1 and 2

6 Silver decoration technique

observed back stress σ_B trend (Fig. 3) and the dislocation arrangement (Fig. 4).

In fact, the increase of mobile dislocations, as they are unpinned from hydrogen, explains the cyclic softening. On the other hand, the hydrogen trapped and accumulated around inclusions, without dislocation assistance, plays a fundamental role in the failure of steel. In this sense, bubbles formed round inclusions promoting matrix inclusion decohesion, i.e. conducting to quasi-cleavage fracture surface observed.

Conclusions

The hydrogen influence on the low cycle fatigue behaviour of high strength steel was studied in terms of friction and back stresses. The following conclusions can be drawn from the present study.

The cyclic behaviour of the hydrogen charged samples is mainly related with the evolution of friction stress component. The hydrogen atoms pin dislocations, producing high friction stress levels. As cycling proceeds, the decrease of the friction stress that is ascribed to the unpinning of dislocations from hydrogen atoms explains the cyclic softening observed.

The back stress does not show a significant difference between the charged and uncharged samples.

The hydrogen accumulated around MnS inclusions is finally responsible for the failure of steel.

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