

# DIFFUSION AND STRAIN-ASSISTED TRANSPORT AND TRAPPING OF HYDROGEN IN FERRITIC STEELS

A.-M. Brass and J. Chêne  
Laboratoire de Physico-Chimie de l'Etat Solide, CNRS UMR 8648  
Bâtiment 410, Université Paris-Sud, 91405 Orsay France

## ABSTRACT

Electrochemical permeation tests were performed during tensile straining of low alloy Cr-Mo steels for investigating the influence of dislocations generated by plastic deformation on the stationary hydrogen flux. The main parameters were the strain, the hydrogen activity and the strain rate. Two different behaviors were observed i.e an increase or a decrease of the steady state flux depending on the electrochemical charging conditions, the plastic strain, the strain rate and the material's microstructure. The decrease of the hydrogen flux can be attributed to dynamic trapping to strain-induced dislocations. However, the increase of the hydrogen flux which was observed at low strain rates and low hydrogen activities, can be ascribed to hydrogen transport by mobile dislocations. On the other hand, the susceptibility of the steels to hydrogen embrittlement was compared with tensile tests for the case of internal, internal + external and external hydrogen generated in the same conditions than those used for permeation tests. The dependence of the ductility loss on dynamic trapping effects clearly appears for both steels strained under a large external hydrogen activity. The large susceptibility to hydrogen embrittlement observed for the normalized steel strained under a low external hydrogen activity could reflect an additional contribution of hydrogen transported by mobile dislocations.

## 1 INTRODUCTION

Whereas the effect of cold work on the diffusion and trapping of hydrogen in iron and ferritic steels is documented (Kumnick[1], Chaudhary[2], Brass[3]), the influence of dynamic straining on the behavior of hydrogen within materials, and the related question of the respective effects of enhanced trapping and accelerated transport of hydrogen by mobile dislocations is still not well established. A mechanism which involves accelerated hydrogen diffusion due to transport by mobile strain-induced dislocations could contribute to accelerated crack propagation or void nucleation and growth encountered in hydrogen service. However the strain dependent behavior of hydrogen is very difficult to isolate from other phenomena which can also control the local amounts of absorbed hydrogen and the theoretical predictions of an enhanced transport of hydrogen by dislocations (Hashimoto[4]) are not supported by many experimental observations, especially in bcc materials. This phenomenon was observed in iron single crystals (Hwang[5]), or in nickel (Kurkela[6]) but could not be evidenced in bcc steels (Kurkela[7], Zakroczymski[8]). The aim of this work is to show that, for some specific microstructural and environmental characteristics, strain-induced accelerated hydrogen transport could be evidenced in a low alloy Cr-Mo steel. The contribution of this mechanism to hydrogen embrittlement, evaluated from tensile tests involving external and/or internal hydrogen, seems however to be too small to be considered as the rate controlling step for the accumulation of hydrogen

in these complex materials which are known to be susceptible to hydrogen assisted cracking.

## 2 EXPERIMENTAL

Low alloy Cr-Mo steels (Table 1) were used for permeation tests during tensile straining and for tensile tests performed after or during cathodic charging. The steels were heat treated to get a ferrite-pearlitic microstructure for the 4120 steel and a bainitic microstructure for the 2.25Cr-1Mo steel.

Table 1 : Chemical composition of 4120 and 2.25Cr-1Mo steel s (wt.pct.)

steel	C	Mn	Si	P	S	Cr	Mo	Ni	Cu	Al	Ti	N	Fe
4120	.19	.66	.22	.018	.014	.95	.18	.16	.20	.029	.004	.001	bal
2.25Cr-1Mo	.13	0.58	.18	.0004	.003	2.2	1.04	0.14	.07				bal

Large flat tensile samples (gauge length 45mm, section width 19 mm, thickness 0.8 mm) were used to study the hydrogen permeation behavior during tensile straining. The samples were mechanically polished up to 1  $\mu\text{m}$  diamond finish on both sides and used without palladium deposition in order to avoid any rupture of the deposit during tensile straining. Electrochemical permeation tests (Devanathan[9]) were conducted by setting a tensile specimen fixed on a tensile machine between the two compartments of a thermostated permeation cell. Cathodic polarization was performed in one compartment either in deaerated 0.1N NaOH at -1350mV/S.C.E. or in deaerated 1N H<sub>2</sub>SO<sub>4</sub> at 5 mA/cm<sup>2</sup>. At steady-state, uniaxial tensile straining was started at a constant applied strain rate of 10<sup>-4</sup>.s<sup>-1</sup>, 10<sup>-5</sup>.s<sup>-1</sup> or 10<sup>-6</sup>.s<sup>-1</sup> and continued in the plastic domain. The stress-strain curves were recorded together with the change of the stationary permeation current. The variables were thus the external hydrogen concentration, the strain rate and the steel microstructural and mechanical characteristics.

Small tensile samples (gauge length 8mm, section width 2 mm, thickness 1 mm) were used for tensile tests conducted at 10<sup>-3</sup> and 10<sup>-4</sup>.s<sup>-1</sup> (i) in air with samples cathodically pre-charged for 5 hours at room temperature in 0.1N NaOH at -1350mV/S.C.E. or in 1N H<sub>2</sub>SO<sub>4</sub> at 5 mA/cm<sup>2</sup> and (ii) during cathodic charging in these conditions of sample either pre-charged for 5 hours or initially free of hydrogen. The role of hydrogen on the fracture mode was investigated by SEM. The hydrogen concentration introduced by cathodic charging was quantified with the melt extraction technique.

## 2 RESULTS AND DISCUSSION

2.1. Dependence of the stationary hydrogen permeation current on strain, strain rate and hydrogen activity.

The electrochemical permeation technique involves the polarization of the detection side of the sample in an alkaline solution in the passive range in order to detect the permeated hydrogen atoms as an oxidation current. Depassivation which occurs from the onset of yielding leads to a strain-induced dissolution reaction of iron and thus to a parasitic anodic current which increases with strain. This depassivation current must be quantified for each strain rate chosen and subtracted from the anodic current representative of the hydrogen permeation changes consecutive to tensile straining.

The dependence on strain, strain rate and cathodic charging conditions is illustrated for the normalized 4120 steel and the bainitic 2.25Cr-1Mo steel in Figure 1. The steady-state value of the permeation current established before tensile straining depends on the charging condition i.e. on the external hydrogen activity. The initial value of the steady-state current is marked in Figure 1 by arrows for each charging condition chosen. The stress-strain curves are plotted as dotted lines.

Cathodic charging from sulfuric acid leads to a much larger hydrogen flux than charging from sodium hydroxide. For the 4120 steel (Figure 1a) and the charging condition which involves a large external hydrogen activity (1N H<sub>2</sub>SO<sub>4</sub>, 5mA/cm<sup>2</sup>), the current decreases from the onset of yielding and with a further increase of the strain

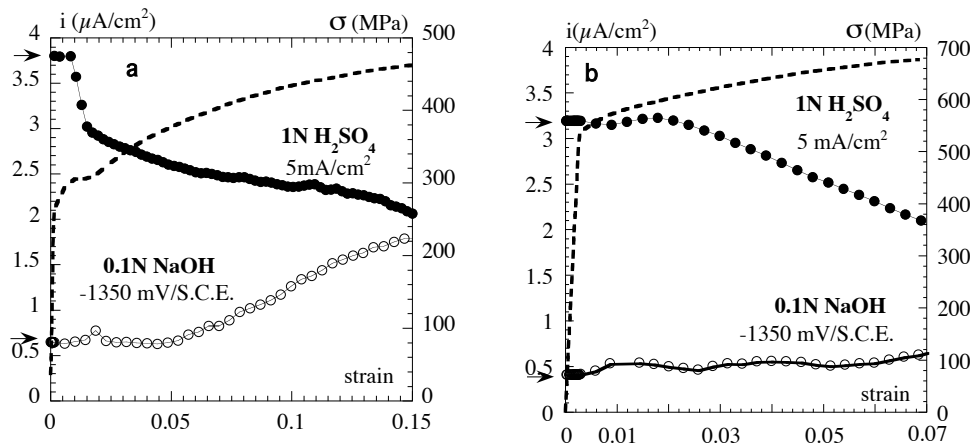


Figure 1. Influence of strain and of cathodic charging conditions on the stationary permeation current during tensile straining at  $10^{-4} \text{ s}^{-1}$ , 298K. a) 4120 steel, b) 2.25Cr-1Mo steel.

In this case the lattice hydrogen concentration can be assumed to be large enough to allow for a significant trapping of hydrogen to newly created dislocations with a large detrapping kinetics (McNabb[10]). This leads to a decrease of the permeability of the steel to hydrogen during tensile straining, due to the so called "dynamic trapping" effect (Hashimoto[4], Tien[11]) of hydrogen to strain-induced immobile dislocations which multiply with a high density upon yielding. This behaviour is in agreement with the few studies of the literature devoted to hydrogen permeation during concomitant tensile straining of bcc steels (Hashimoto[4], Kurkela[7], Zakroczymski[8]).

For the bainitic 2.25Cr-1Mo steel (Figure 1b), the strain-induced change of the stationary permeation current compares with that of the 4120 steel for charging from 1N  $\text{H}_2\text{SO}_4$ , except that the magnitude of the current decrease is smaller. This can be ascribed to differences in the dislocation mean free path, in the respective rates of dislocation generation and hydrogen trapping to these dislocations which are controlled by the material's microstructure and the mechanical properties. In this bainitic steel, only a predominant effect of strain-induced dynamic trapping was observed.

For cathodic charging from 0.1N NaOH which corresponds to a low external hydrogen activity, a peak is observed at the onset of yielding for the 4120 steel (Figure 1a). This peak can reflect a contribution to the hydrogen current of hydrogen transported by dislocations along the slip bands associated, in the yield point elongation domain, with high local strain rates and with a large mean free path for the mobile dislocations generated by plastic deformation. Moreover, contrary to the current vs strain behavior observed for the largest hydrogen activity, the permeation current continuously increases with deformation from the end of the easy glide domain. As expected, the slower the strain rate the smaller the peak observed at the onset of yielding (Figure 2a), in concordance with a mechanism involving hydrogen transport by mobile dislocations. The quasi invariability of the steady-state flux at low strain rate ( $10^{-6} \text{ s}^{-1}$ ) (Figure 2a) can be explained by an increasingly large probability of interaction between trapped and lattice hydrogen when the dislocation velocity decreases. Since the change of the cathodic current associated with charging in 0.1N NaOH at  $-1350 \text{ mV/S.C.E.}$  is small in the strain range considered, the large increase of the stationary permeation current with the strain can be ascribed to a contribution of an enhanced transport of hydrogen by strain-induced mobile dislocations, a small lattice diffusivity and concentration, and a large dislocation velocity (Kitagawa[12]). As cathodic charging in 0.1N NaOH at  $-1350 \text{ mV/S.C.E.}$  involves a small lattice hydrogen concentration, a small capture rate of hydrogen atoms by newly generated dislocations can be anticipated, especially in the region near the output surface of the tensile specimen where a near to zero lattice concentration is imposed. For this

charging condition and for the 4120 steel's microstructure considered, dynamic trapping effects can thus be considered to be small.

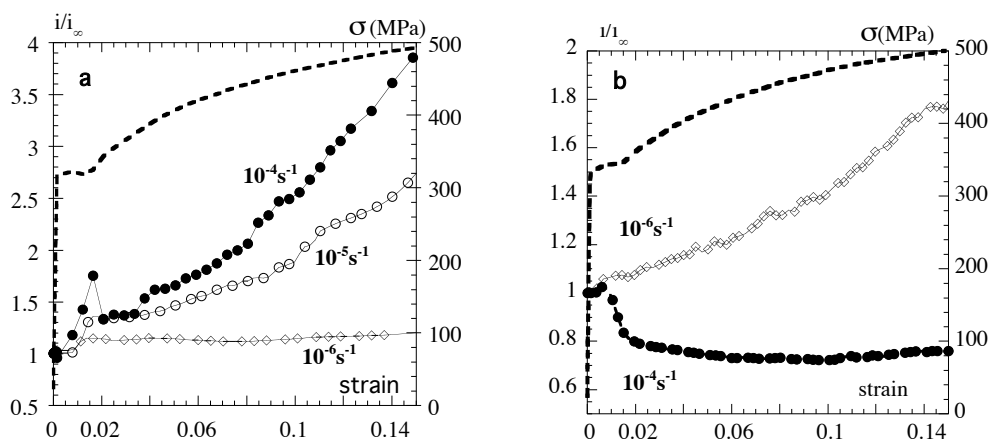


Figure 2. Influence of strain and strain rate on the stationary permeation current through 4120 steel normalized with respect to the initial value of the stationary current. a) cathodic charging from 0.1N NaOH (-1350 mV/S.C.E), 298 K. b) cathodic charging from 1N H<sub>2</sub>SO<sub>4</sub> (5mA/cm<sup>2</sup>, 298 K).

Furthermore, at high strain rates, a large density of mobile dislocation with a large mean velocity is certainly easily generated in the normalized microstructure of the 4120 steel for which a low initial dislocation density and a large mean free path for mobile dislocations can be assumed. As a consequence, a large fraction of hydrogen could be trapped with a small detrapping kinetics (McNabb[10]) to freshly created dislocations. The contribution to the permeation current of hydrogen transported by mobile dislocations would thus be possible and more detectable at larger strain rates. However, a large capture rate of hydrogen by dislocations associated with a large hydrogen activity, a low rate of dislocation generation with a large mean free path of mobile dislocations transporting large amounts of hydrogen can also account for reduced dynamic trapping effects and for the increase of the stationary current observed for the 4120 steel during concomitant tensile straining at  $10^{-6} \text{ s}^{-1}$  and cathodic charging from H<sub>2</sub>SO<sub>4</sub>N (Figure 2b).

## 2.2. Dependence of the susceptibility to hydrogen embrittlement on charging conditions and strain rate.

In order to attempt to correlate the role of tensile straining on the permeability to hydrogen with the ductility loss of hydrogen charged specimens, tensile tests were performed at room temperature by changing either the hydrogen activity ( $a_H$ ) on the specimen surface or the strain rate. The hydrogen activity associated with tests conducted in air, which can be considered to be very low, yields 50-100 atm for cathodic charging from 0.1N NaOH and about 1500 atm when cathodic charging is conducted in 1N H<sub>2</sub>SO<sub>4</sub> for the electrochemical conditions chosen (Brass[3]). An embrittlement index (E.I.) representative of the hydrogen-induced ductility loss was computed by comparing the uniform and the total elongation of hydrogen charged and hydrogen free specimens. The results reported in Figure 3 illustrate the role of different testing conditions on the hydrogen-induced elongation loss measured for the two steels.

The normalized 4120 steel pre-charged from 1N H<sub>2</sub>SO<sub>4</sub> and then strained up to rupture in air exhibits a very small ductility loss (Figure 3a) whereas a clear decrease of the uniform and total elongation is observed when an external hydrogen activity is applied during tensile straining. Since an increase of  $a_H$  leads to an increase of the trap occupancy fraction, this observation suggests a strong influence of hydrogen interactions with strain-induced defects since those defects present before

straining do not induce a significant hydrogen embrittlement. The much larger effect of hydrogen on the total elongation reflects an increase of the embrittlement after necking, which can be ascribed to the interaction of hydrogen with strain induced microvoids. From the change of the stationary hydrogen flux during simultaneous plastic deformation (Figure 1) and cathodic charging from 1N H<sub>2</sub>SO<sub>4</sub>, an increase of the susceptibility to hydrogen embrittlement can be expected due to dynamic trapping of hydrogen to strain-induced defects.

The respective influence of internal and external hydrogen on the ductility loss can be evaluated from tensile tests performed during cathodic charging with or without hydrogen pre-charging of the specimens. Hydrogen free samples strained in the presence of an external hydrogen activity and hydrogen pre-charged samples further strained under cathodic charging exhibit a similar ductility loss. This observation reflects a predominant role of external hydrogen on the susceptibility to hydrogen embrittlement. However when the strain rate is too large to allow for a significant hydrogen absorption during tensile straining of the initially hydrogen free specimens under a low external hydrogen activity (tensile straining in 0.1N NaOH at 10<sup>-3</sup>s<sup>-1</sup>), the uniform ductility loss is, as expected, very small due to the limited extent of the hydrogenated zone and the small trap occupancy fraction.

As shown by Figures 1 and 2, increasing  $\dot{\epsilon}_t$  will favor the dynamic trapping of hydrogen and consequently the interaction of diffusible hydrogen with strain-induced defects. The susceptibility to hydrogen embrittlement will thus increase if the time allowed for hydrogen diffusion is not too short. On the opposite, at the strain rates chosen, decreasing  $a_H$  will lead to an increase of the diffusible hydrogen concentration with a possible contribution of dislocation transport. In this case, a redistribution of internal hydrogen in pre-charged samples can account for the comparatively large uniform ductility loss measured with the samples strained at 10<sup>-4</sup>s<sup>-1</sup> while exposed to cathodic charging in 0.1N NaOH in comparison with the ductility loss resulting from tensile straining during cathodic charging with a larger hydrogen activity (1N H<sub>2</sub>SO<sub>4</sub>).

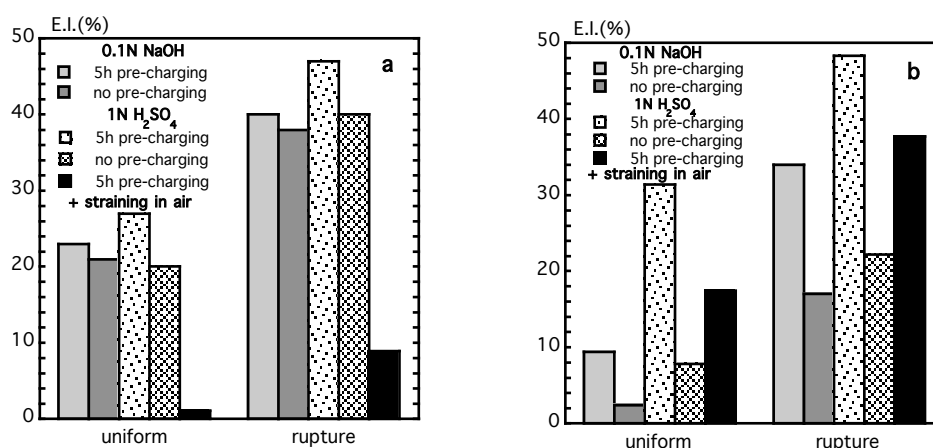


Figure 3. Influence of hydrogen charging conditions on the embrittlement index computed from the uniform and total elongation loss of a) 4120 steel, b) 2.25Cr-1Mo steel (10<sup>-4</sup>s<sup>-1</sup>, 298 K).

In comparison with the 4120 steel, a different behavior is observed for the hydrogen pre-charged 2.25 Cr-1Mo steel which exhibits a significant hydrogen-induced embrittlement when strained in air (Figure 3b). Hydrogen trapping on pre-existing defects is presumably the main mechanism responsible for the hydrogen-induced ductility loss as attested by the fracture surfaces (fisheyes initiated on non metallic inclusions). The increase of the embrittlement index with the external hydrogen activity observed for samples initially free of hydrogen can be ascribed both to the dependence of the hydrogen

diffusivity on the hydrogen concentration (Brass[3]) and to the larger diffusible hydrogen trap occupancy resulting from an increase of the external hydrogen activity. For samples pre-charged with hydrogen and then strained under cathodic charging, the larger ductility loss measured for the tests performed with the acidic charging solution can be attributed to the saturation of the pre-existing traps resulting from a larger diffusible hydrogen concentration but also to the dynamic trapping of hydrogen evidenced during concomitant permeation and straining tests (Figure 1b). As a matter of fact, this effect only can explain why samples precharged from 1N H<sub>2</sub>SO<sub>4</sub> are more brittle after straining in the acidic solution than in air.

In comparison with the 4120 steel, the embrittlement index determined after charging from 0.1N NaOH is systematically smaller than that derived from tests performed in the acidic solution; This observation can be related with the negligible influence of dynamic trapping and strain assisted transport by dislocations when the hydrogen activity is low, as shown by the invariability of the permeation current during tensile straining in the uniform deformation range (Figure 1b).

#### 4 SUMMARY

Permeation tests were performed with a normalized 4120 steel and a bainitic 2.25Cr-1Mo steel during concomitant tensile straining. For both steels, hydrogen trapping on newly generated immobile dislocations leads to a decrease of the stationary hydrogen flux at 10<sup>-4</sup>s<sup>-1</sup> for a large external hydrogen activity. At high strain rates, a strain-induced increase of the permeation current was observed for a low external hydrogen activity only for the 4120 steel. This effect can be ascribed to an enhanced transport of hydrogen by mobile dislocations.

The dependence of the susceptibility to hydrogen embrittlement on external and internal hydrogen activity was evaluated with tensile tests conducted with hydrogen free or hydrogen pre-charged specimens during electrochemical charging. For both steels, the contribution of dynamic trapping to the ductility loss can clearly be evidenced for tests performed with a large hydrogen activity. The contribution of strain-assisted transport of hydrogen by mobile dislocations in the normalized steel can be evidenced by the large influence of a low external hydrogen activity on the embrittlement of this steel.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- [1] Kumnick J. and Johnson H.H., Hydrogen transport through annealed and deformed Armco iron, *Met Trans*, 6A, 1199-1206 (1974).
- [2] Chaudhary R.S. and Riecke E., *Werkstoffe und Korrosion* 32, 73-78 (1981).
- [3] Brass A.-M, Guillon F. and Vivet S., *Metal. and Mater. Sci Trans.*, 35A, 1449-1464 (2004).
- [4] Hashimoto M. and Latanision R.M., *Acta Metall.*, 36 (7) 1837-1854 (1988).
- [5] Hwang C. and Bernstein I.M., *Acta Metall.*, 34 (6), 1001-1010 (1986).
- [6] Kurkela M. and Latanision R.M., *Scripta Met.*, 13, 927-932 (1979).
- [7] Kurkela M., Frankel G.S., Latanision R.M., Suresh S. and Ritchie R.O., *Scripta Met.*, 16, 455-459 (1982).
- [8] Zakroczymski T., *Corrosion-NACE*, 41 (8), 485-489 (1985).
- [9] Devanathan M.A.V. and Stachurski Z., *J., Electrochem. Soc.*, 111(5), 619-623 (1964).
- [10] McNabb A. and Foster P.K., *Trans. Metall. Soc AIME*, 227, 618-627 (1963).
- [11] Tien J.K., Thompson A.W, Bernstein I.M. and Richards R., *Met Trans.*, 7A, 821-829 (1976).
- [12] Kitagawa H. and Kojima Y. *Atomistics of fracture*, Latanision R.M., Pickens J.R. Editors, NATO conf. Series, Plenum press New York, p. 799 (1983).