

# Mechanical and electrochemical alteration of sorbitic and austenitic steels charged with hydrogen

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## Abstract

Experiments made with the method initiated by Hyspecka and Mazanek (1) have revealed phenomena not encountered with other methods of investigation, such as the recovery of mechanical properties while still discharging, and the simultaneous effect on electrochemical voltage, which can only be due to a transformation of the hydrogen state inside the metal.

It was also observed experimentally that those processes are generalized, may be iterative, and occur for times correlated with the density of discharge.

An attempt was also made, with very significant results, to correlate the variation in these mechanical properties, depending on the hydrogen charging time, with the much more easily achieved variation in electrochemical characteristics. Study of these phenomena was combined with examination of the fracture surfaces and numerous longitudinal diametral sections under the fractures, using a Cambridge 600 scanning electron microscope (SEM).

The results for sorbitic steels were published as they became available (2-8) and an interpretative model was proposed based on them; the new results for austenitic steels, and for electrochemical tests, also seem capable of being referred to that model.

Even though the model constitutes a hypothesis needing verification, it seems suitable for giving semi-quantitative assessments in the study of phenomena not hitherto reported in the scientific literature.

At all events, in terms of application, the series of experiments on austenitic and sorbitic steels already allow conclusions to be drawn about when they are most suitable for use in highly hydrogenating environments.

## Riassunto

### Alterazioni meccaniche ed elettrochimiche di acciai sorbitici ed austenitici sotto carica di idrogeno.

Esperienze condotte con il metodo iniziato da Hyspecka e Mazanek (1) hanno permesso di evidenziare fenomeni, non riscontrati con altri metodi di indagine, quali il recupero delle caratteristiche meccaniche ancora sotto scarica, e la simultanea alterazione della tensione elettrochimica, che possono essere dovuti solo a una trasformazione dello stato dell'idrogeno all'interno del metallo.

Inoltre, si è potuto constatare sperimentalmente che questi processi sono generalizzati, possono avere andamento iterativo, e si riscontrano per tempi correlati alla densità di scarica.

Si è cercato anche di correlare, con risultati molto significativi, la variazione di queste caratteristiche meccaniche, in funzione del tempo di carica di idrogeno, alla variazione di caratteristiche elettrochimiche (di realizzazione molto più agevole). Lo studio di questi fenomeni è stato integrato con l'esame delle superfici di frattura e di numerose sezioni longitudinali diametrali, a ridosso della frattura, con l'uso del Microscopio Elettronico a Scansione (Cambridge 600).

Sulla base dei risultati relativi agli acciai sorbitici, resi pubblici man mano che venivano ottenuti (2-8), si è proposto un modello interpretativo, al quale sembrano potersi riportare anche i nuovi risultati relativi agli acciai austenitici ed alle prove elettrochimiche.

Anche se questo modello costituisce soltanto una ipotesi da verificare, esso appare atto a dare delle valutazioni semi-qualitative in una fenomenologia finora non segnalata nella letteratura scientifica.

Comunque, sul piano applicativo, le serie di esperienze condotte sugli acciai austenitici e sorbitici permettono già di giungere a conclusioni circa le opportunità migliori per il loro impiego in ambienti fortemente idrogenanti.

## Introduction

Owing to the requirements of the energy and chemical industries, and the petroleum chemical industry in particular, steels with a high elastic limit are being subjected to high loads in hydrogen-rich environments with increasing frequency. These are conditions that produce strong interactions between the steel and hydrogen, which in different forms and at different rates, depending on the environment and the lattice, tend to penetrate the steel and affect its mechanical properties. The problem of interaction between steel and hydrogen therefore arises now in a way completely different from the way in which it has been studied in earlier decades, when the residual hydrogen content of steel at the end of refining was what mattered.

By using the premature fracture method devised by Hyspecka and Mazanek (1) it is possible to examine the course of the phenomena when there is a concentration gradient, that is, in conditions close to those found in operation when the material is placed between a hydrogen-rich environment and the atmosphere, as happens in pipelines, containers and the like.

Because of this, the experiments (2-8) did not include any measurements of the testpieces' hydrogen content after charging, since they would simply have resulted in

an evaluation averaged on an unknown distribution. On the other hand, both the discharge density (which, according to the formula  $P = 17i$ , with  $i = \text{mA/cm}^2$ , corresponds to a given external hydrogen pressure) and the discharge duration were always determined, as they condition the progress of hydrogen distribution inside the circular-section bar.

## Test materials and techniques

Research was done on three types of steel, namely:

- 38 NiCrMo4 heat-treatable steel to UNI 5332-64, a widely used industrial steel with two phases (b.c.c and compact rhombic lattices), hardened and tempered, in the sorbitic state.
- X8CrNi 1910 steel to UNI 6900, an austenitic stainless steel much used in the chemical industry on account of its excellent resistance to chemical agents in general, and regarded as almost unaffected by hydrogen attack; it has a single phase with c.f.c. lattice.

Table 1 shows the chemical composition of the two steels.

Preliminary tests were also made on a chromium ferritic steel having practically a single phase, with b.c.c. lattice.



**TABLE 1 - Chemical composition of the two steels used.**

Chemical analysis	C	Ni	Cr	Mo	Mn	Si	S	P
38 NiCrMo4	0.38	0.72	0.81	0.16	0.76	0.32	0.024	0.010
X8CrNi1910	≤0.08	8.00	19.00	—	≤ 2	0.01	0.03	0.045

Stress-corrosion test bars, ground over the gauge length, were used for both the premature-fracture and the electrochemical tests (Figure 1).

In the premature-fracture tests, the testpiece is subjected to electrolytic hydrogenation, using cathode discharge with a decinormal solution of  $H_2SO_4$  (detail in Figure 2) at constant current density for various times. Then, when hydrogenation has been stopped and the preload is removed, after a standard time of 3 min the piece is subjected at ambient temperature to tension at constant rate of deformation.

A constant-load stress-corrosion machine (Fig. 2) and an Instron tensile testing machine were used for the tests.

For the electrochemical tests, an Amel 551 potentiostat applied to a stress-corrosion machine, was used.

Fig. 1 - Premature-fracture test bar.

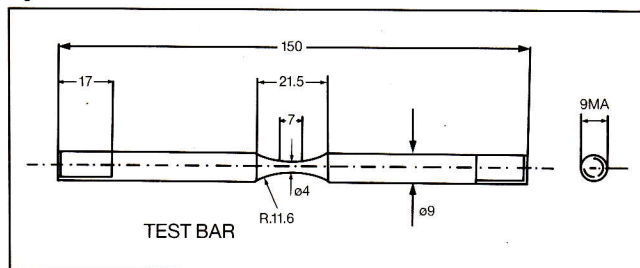
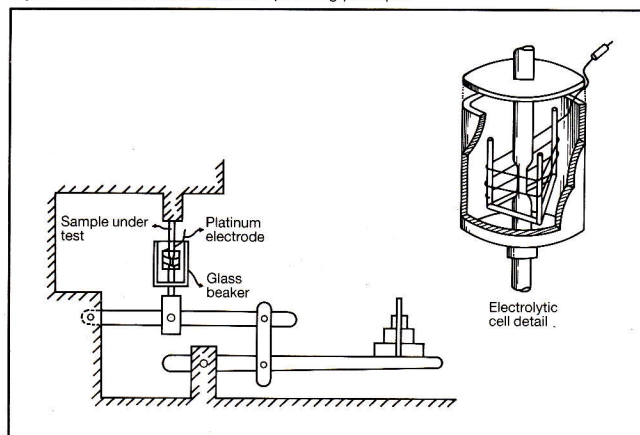


Fig. 2 - Stress corrosion machine operating principle.



The interaction of hydrogen with the steel is recorded mainly by the effect on the value of:

- The reduction of area.
- The ultimate tensile stress.
- The fracture surfaces.
- The cathode discharge potential.

## Results

### Premature-fracture tests

These were done as follows:

(1) For the 38 NiCrMo4 steel:

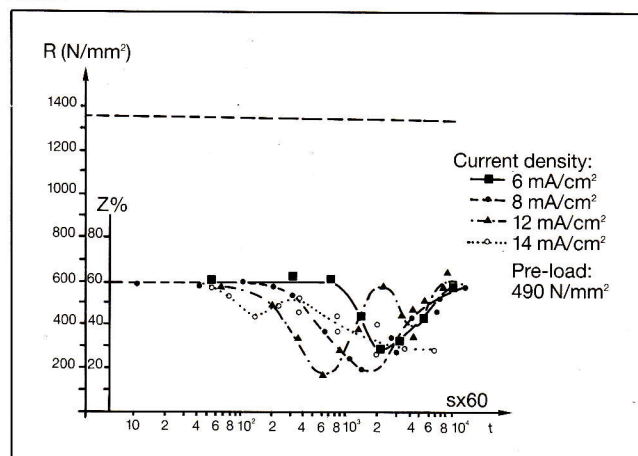
- Maintaining a fixed preload of 490 N/mm<sup>2</sup> and varying the discharge densities (6, 8, 12 and 14 mA/cm<sup>2</sup>) (Figure 3).
- Maintaining a fixed discharge density of 8 mA/cm<sup>2</sup> and varying the preloads (490, 524 and 568 N/mm<sup>2</sup>) (Figure 4).

(2) For the X8CrNi 1910 steel:

- At a preload of 550 N/mm<sup>2</sup> and varying discharge densities of 8, 14 and 16 mA/cm<sup>2</sup> (Figure 5).

Tests were not made at preloads higher than 550 N/mm<sup>2</sup>, which is already well above the yield point, with plastic deformation so high that, at the grain size of our samples, considerable surface damage under the preload could be seen. Nor were any tests made at

Fig. 3 - Steel 38 NiCrMo4; current density: (6, 8, 12, 14) mA/cm<sup>2</sup>; pre-load: 490 N/mm<sup>2</sup>.





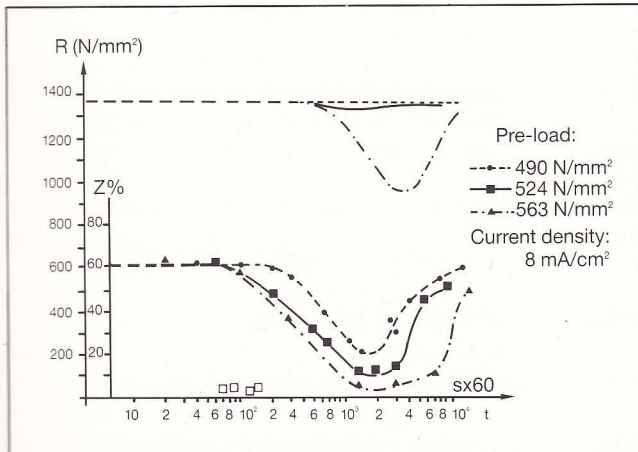


Fig. 4 - Steel 38 NiCrMo4; pre-load: (490, 524, 563) N/mm<sup>2</sup>; current density: 8 mA/cm<sup>2</sup>.

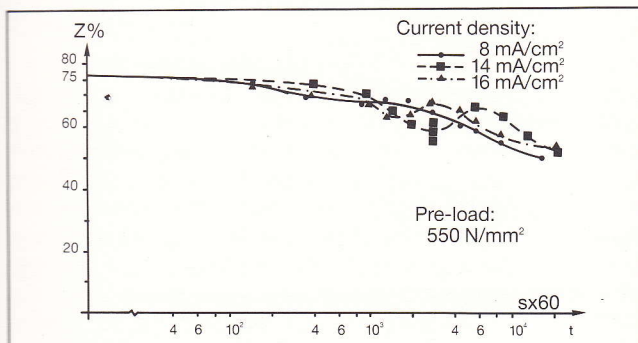


Fig. 5 - Steel X8CrNi 1910; current density: (8, 14, 16) mA/cm<sup>2</sup>; pre-load: 550 N/mm<sup>2</sup>.

preloads lower than 300 N/mm<sup>2</sup>, because even at that preload no fall in the reduction of area was found.

From examination of the results, the following points emerged for both steels:

- For a given discharge density and applied preload there are effects on the mechanical properties of reduction of area, which reach a maximum, continue for discharge periods of varying length, and then give rise to a recovery of the mechanical properties (still under discharge), which is total for the 38 NiCrMo4 steel and incomplete, but still clearly observable, for the X8CrNi 1910.
- A further fall in the reduction of area occurs later, with discharge still continuing.
- There is a clear correlation between discharge density and stress: for constant discharge densities, the times at which maximum damage commences are almost constant; when the stress is varied, there are changes in the rate of maximum alteration in the reduction of area.

For the 38 NiCrMo4 steel two further points were

noted:

- For loads between the yield point and the ultimate tensile stress there is a dispersion band within which all the samples reach fracture, in fairly short times that decrease statistically as the load increases.
- At stresses close to the yield point there are reductions in the ultimate tensile stress, with times of commencement of maximum damage close to those of the fall in reduction of area, and fracturing under electrochemical discharge, always occurring at times close to those of commencement of the decrease in reduction of area (almost as if involving a critical condition of the material) accompanied by a higher inclusion state of the material.

When the samples that had a nett recovery of mechanical properties were examined under the SEM the following points were noted:

- In the 38 NiCrMo4 steel there is permanent alteration consisting of holes that coalesce together to form actual channels (9) (Figure 6), with no

Fig. 6 - 38 NiCrMo4 steel. Pre-load 490 N/mm<sup>2</sup>. Current density 14 mA/cm<sup>2</sup>. Charging time 2500. a)  $\times 50$ ; b)  $\times 1000$ .





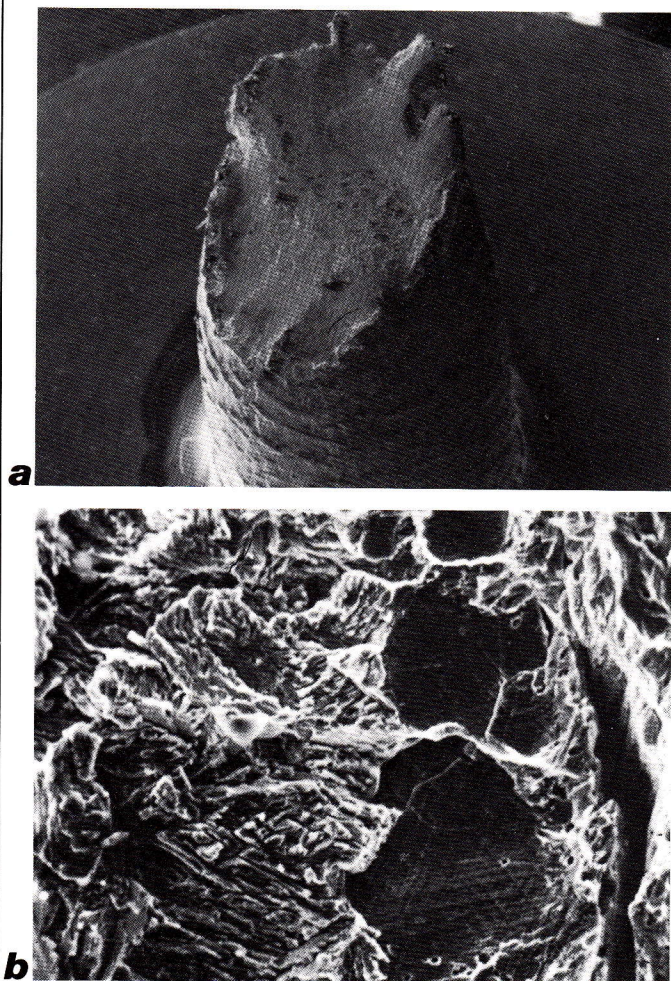


Fig. 7 - X8CrNi 1910. Pre-load 550 N/mm<sup>2</sup>. a) Current density 14 mA/cm<sup>2</sup>; charging time 1500 ( $\times 20$ ). b) Current density 16 mA/cm<sup>2</sup>; charging time 5700 ( $\times 500$ ).

noticeable degradation of the surface of the material.

— In the X8CrNi 1910 steel, on the other hand, there is deep "sclerotization" of the surface after hydrogenation (Figure 7), showing that hydrogen has penetrated, though with difficulty, into the steel's lattice, but is mainly localized at the grain joints.

This deep sclerotization leads to a reduction in the load-resisting cross section and prevents the material from recovering its initial reduction of area. Yet the incidence of this phenomenon is slight, bearing in mind that the thickness involved is of the order of 0.1 mm and that this limitation does not work out at more than 1%.

### Electrochemical tests

The electrochemical tests revealed alteration of the material, identified by variations in potential, for the

same discharge times as those at which the mechanical properties changed.

It will be seen in Figure 8 how the decrease in reduction of area is matched by an increase in electrochemical potential, for the X8CrNi 1910 steel at 14 mA/cm<sup>2</sup> with a preload of 550 N/mm<sup>2</sup>.

It is also important to note that both phenomena, reduction of area and supersaturation, have the same range.

### Interpretation of results

During the discharge process, hydrogen penetrates from the testpiece surface, under which a supersaturation zone is formed whence the hydrogen atoms that have penetrated tend to diffuse inwards. Joints between grains and dislocations are the preferred routes for diffusion.

When the free energy of the system is favourable, particularly in zones of discontinuities or impurities, which act as catalysts, there is transition of the hydrogen to molecular form (10).

This process removes hydrogen from the subsurface zone and facilitates further penetration.

In the specific case of the 38 NiCrMo4 the hydrogen molecule tends to form at already existing cavities, (particularly if catalysing inclusions are present), where they generate extremely high pressure, though it corresponds to a lower energy content of the system than that for distortions caused by the presence of hydrogen ions in solution.

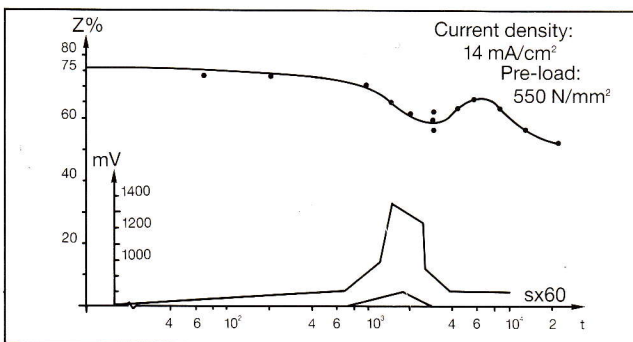


Fig. 8 - Steel X8CrNi 1910 electrochemical test. Current density: 14 mA/cm<sup>2</sup>; pre-load: 550 N/mm<sup>2</sup>.

The "mean" diffusion coefficient (11) for the two steels is very different, being 10<sup>3</sup> to 10<sup>4</sup> times as high for the sorbitic steel as for the austenitic steel.

Nevertheless, these "mean" coefficients should be regarded as resultants of diffusivity through the mass, which differs strongly in the two cases, as ferrite has a b.c.c. lattice and austenite a c.f.c. lattice (12-14), and also through the core of dislocations and the inter-grain



joints, in which the two materials differ much less. Consequently, hydrogen flow in polycrystalline austenitic steel occurs in a substantially different form from the flow in sorbitic steel, as it is mainly localized at the inter-grain joints and the planes containing the greatest number of dislocations (planes of maximum stacking).

For a given hydrogen flow, therefore, in sorbitic steel there will tend to be a network of little channels, varying in density according to the state of the inclusion and the discharge density, with damages almost totally recoverable by degassing, whereas in austenitic steel less damage will be found, though more serious because irreversible, revealed as surface sclerosis, as little channels and as surfaces of intergranular decohesion, where stacking is at its greatest in the sclerotized zone.

## Conclusions

Austenitic steels also appear susceptible to damage by a hydrogenating atmosphere. However, though they suffer intense and irreversible attack, this is localized at the surface, and they therefore appear particularly suitable for constituting screens against hydrogen penetration into sorbitic steels, which suffer a damage almost completely reversible but very dangerous because, in particular conditions, it can cause embrittlement throughout the structure.

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