

IDENTIFICATION OF THE DAMAGE IN HIGH STRENGTH STEELS AFTER ELECTROCHEMICAL HYDROGEN CHARGING

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ABSTRACT

Multiphase steels are quite sensitive to hydrogen embrittlement. Laboratory tests to evaluate this often use electrochemical charging to introduce hydrogen into the sample, but damage purely caused by hydrogen charging has to be avoided.

A ferrite-bainite steel was charged using various conditions to identify when surface blisters occurred. Samples were also checked for internal damage by electron microscopy.

This study was repeated for three other multiphase steels and pure iron. An HSLA steel was found to be more resistant whereas pure iron was quite susceptible to internal hydrogen damage. For all industrial steels, cracks concentrated in the middle of the sample were attributed to inclusions and segregations, inherent to production.

INTRODUCTION

The harmful consequences of the exposure of steel to a hydrogen containing environment were first discussed by Johnson [1]. It was shown in his work that hydrogen caused a decrease in ductility leading to the phenomenon of hydrogen embrittlement. High strength steels turn out to be even more sensitive to this type of embrittlement. Nowadays, the use of high strength steels in hydrogen rich environments becomes increasingly important in industry. Therefore, a detailed study of the interaction between hydrogen and these steels is a prerequisite to be able to predict the potential damage (hydrogen blisters, hydrogen induced plasticity loss, hydrogen embrittlement and hydrogen induced cracking).

Blisters appear in many materials in the absence of external stress when the hydrogen concentration is high enough. Most mechanisms suggest that hydrogen atoms combine into hydrogen gas molecules at the interface of second phase and matrix, producing high hydrogen pressure which induces microcracks. The propagation and connection of these microcracks induces blisters and cracks formation. [2]. Over the past decades, the effects of hydrogen and hydrogen blister formation on the corrosion of traditional materials such as iron, stainless steel, pipeline steel, aluminum and nickel alloys have been extensively studied [3, 4, 5]. It was found that during corrosion or stress corrosion cracking (SCC) of magnesium and its alloys, hydrogen may exist in three states on the surface, or in the matrix: as hydrogen atoms, as hydrogen gas and as hydride. After immersion and cathodic charging in 0.1 M NaOH, the state of hydrogen in the interior of the AZ91 alloy was investigated using secondary ion mass spectroscopy (SIMS) [6]. The investigations described that hydrogen atoms, hydrogen gas and hydride might coexist in the matrix. It was also found after cathodic charging, that most of the hydrogen blisters were located on the primary α -Mg region. When the sample was charged for a longer time, many blisters were formed and many micro-cracks initiated around the ruptured blisters, implying that the two processes are connected.

Cracks are another type of damage.; Hydrogen induced cracking (HIC) occurs in steel if there is a susceptible microstructure and sufficient diffusing hydrogen atoms to initiate and propagate damage. All steels have a unique critical or threshold value of H atom concentration for the initiation of hydrogen damage. The cracks more often lie parallel to the rolling plane and to the surfaces of the steel structure. Blisters often occur when the hydrogen induced crack is unable to propagate further in the direction parallel to the surface. [7].

A relationship appears to exist between the susceptibility to HE and the ability of different microstructural features in the steel to trap hydrogen. The slower the diffusion of hydrogen the more efficient are the traps and the greater is the possibility of forming and developing hydrogen collectors. It is energetically more favorable for hydrogen to stay in a trap site than in a normal lattice interstitial position at temperatures below 300°C [8]. Many types of structural defects can act as traps such as microvoids, grain boundaries, dislocations, precipitates, etc. The most effective trap sites have been discussed by many authors. Pressouyre and Bernstein [9] considered non metallic inclusions (TiC and MnS) as strong irreversible trap sites in steel, and they concluded that if many fine irreversible trap sites were uniformly distributed, the steel would have an increased HE resistance because the trap sites would prevent the transport of hydrogen to the crack tip.

Villalba *et al.* [10] studied the SCC resistance in materials with different microstructure. They found that the steel microstructure in two specific steels and their SCC and HE resistance did not agree with the theory. It was expected that the carbides present in the tempered martensite in one of the samples, would provide a greater number of more efficient trap sites than the grain boundaries and pearlite bands in the pearlitic-ferritic steel. However, both microstructures presented similar behavior in a hydrogen charging environment. Therefore the susceptibility to HE and SCC seems a very specific feature of steel such as microstructure and associated trap sites, the size distribution of inclusions and the strength properties.

In this study, samples of pure iron and a high strength steel (FB450) were charged cathodically at different current densities and during different times, the appearance of blisters at the surface of the sample was then checked in order to develop a “blister mapping”. This allowed us to study and compare the effect of the electrolyte on the charging, the effect of the surface roughness of the sample and even to compare different materials.

We found that this blister mapping could be a quite simple way to be used in hydrogen research because it allows to compare easily different materials as well as other relevant factors on hydrogen embrittlement.

EXPERIMENTAL

Materials

Four different types of multiphase high strength steels were used in this study as well as pure iron as a reference base material. The chemical composition of the materials is summarized in Table 1. FB450 is a ferritic-bainitic steel; TRIP700 is a multiphase steel containing ferrite, bainite and retained austenite; DP600 is a ferritic-martensitic dual phase steel; S550MC is a high strength low alloy steel that contains ferrite, pearlite and Ti-Nb based precipitates;

Table 1: Chemical composition of the materials used (weight percent).

Material/Element	C	Mn	Si	Other
FB450	0.07	1.00	0.10	0.5%-1.0% Cr
TRIP700	0.17	1.60	0.40	1%-2% Al 0.04%-0.1% P
DP600	0.07	1.50	0.25	0.4%-0.8% Cr + Mo
S550MC	0.07	0.95	0.0	0.08%-0.12% Ti + Nb
Pure Iron	0.0015	0.0003	0.0	< 0.02 Al, P

Pure iron specimens were produced in a Pfeiffer VSG100 vacuum melting and casting unit, operated under a protective argon gas atmosphere. Pure iron was processed by hot and cold rolling to sheets of 1.8mm thickness. The sheets were annealed in a salt bath at 750°C for 30 seconds. The grain size was determined by the linear intercept method and was found to be around 30µm.

Circular samples of 20mm diameter of all the materials were punched. The discs of the TRIP700 were ground to 0.65mm thickness because its original commercial thickness is 0.70mm. The other materials were ground to 1.00mm. All materials were ground using a Ziersch & Baltrusch surface grinder with an aluminum oxide stone grinding wheel rotating at 3100rpm.

Blister mapping

In order to compare the blister appearance between two materials, ground discs of FB450 and pure iron, both with 1mm thickness and 2 cm diameter were charged cathodically in a polycarbonate cell between two symmetric Pt anodes. The electrolyte used in the tests is an arsenic aqueous solution (0.5g As₂O₃ – 0.25g HgCl₂ – 60mL H₂SO₄ / 1L H₂O). The samples were charged at room temperature during different times (5, 10, 20 and 30min; 1, 2, 4, and 8 hours; 1, 2 and 3 days) and using different current densities (0.8, 2, 5, 10 and 50 mA/cm²). After charging, the samples were cleaned with distilled water and acetone to remove possible surface deposits. The samples surface was eye-checked to identify possible blisters.

To compare the effect of the electrolyte on blister appearance, ground pure iron discs were charged in the same conditions (time and current density) as mentioned before with two other electrolytes: 5g/L of Thiourea in 0.5M H₂SO₄ and 10g/L of Thiourea in 0.1M NaOH [11].

Crack propagation

In order to study the crack propagation on different materials, ground samples of the four multiphase steels and pure iron were charged at $10\text{mA}/\text{cm}^2$ for 1 hour, 1 day and 3 days using the arsenic-based electrolyte. The cross sections were analyzed by optical microscopy and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Materials characterization

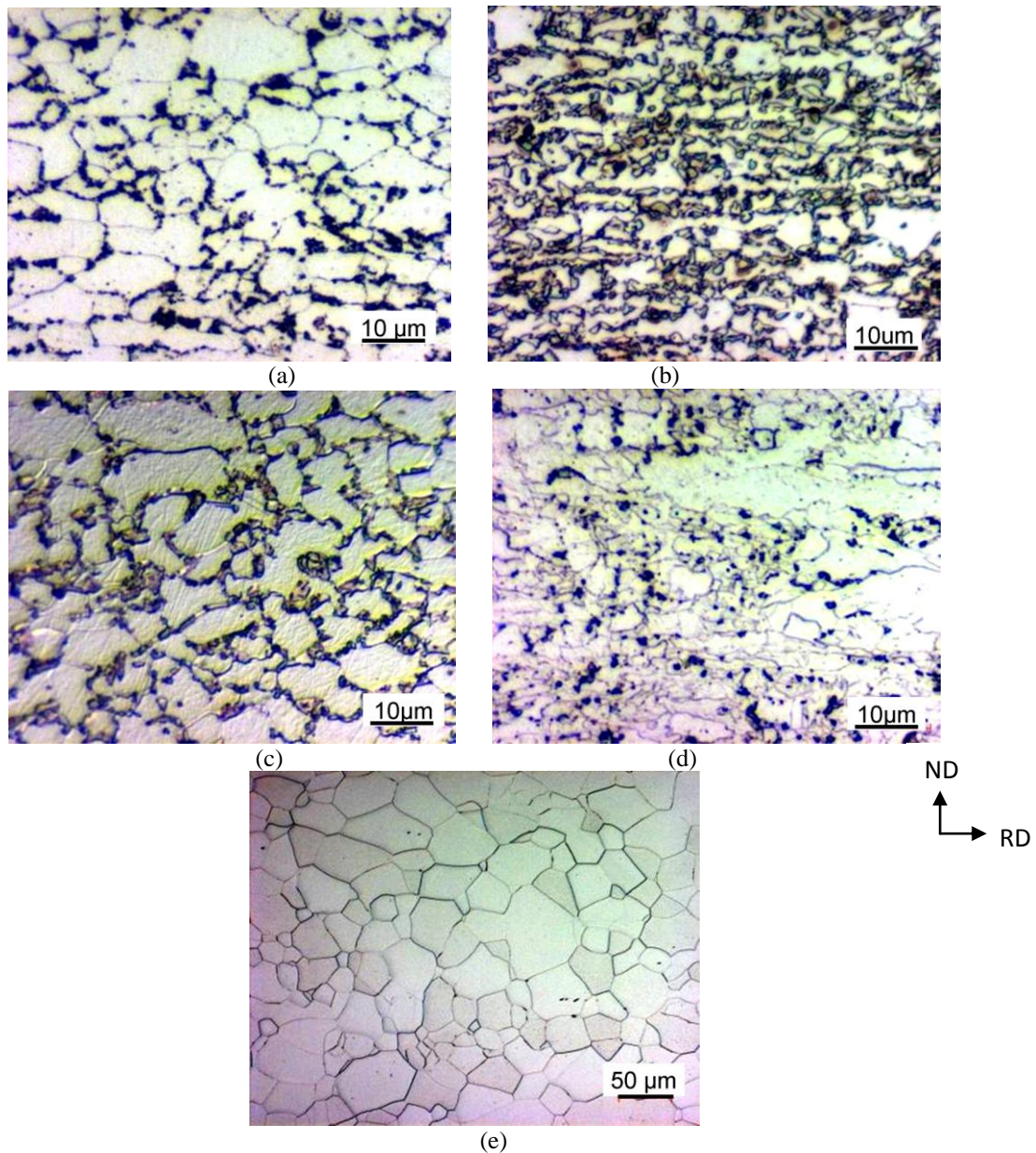


Figure 1. Optical microscopy of the materials microstructure. Nital 2% etching.
(a) FB450 (b) TRIP700 (c) DP600 (d) S550MC (e) Pure Iron

Figure 1 presents the microstructure of the materials used in this work before these materials were charged with hydrogen.

Blister mapping on different materials

Table 2 shows the results of the FB450 mapping after charging with the arsenic-based electrolyte. Each position in the table represents a sample that was charged using a specific current density and during certain time. The empty places denote samples that did not show surface blisters after charging. On the other hand, the X marked areas represent charging conditions that displayed blisters at the surface after charging.

Table 2. Blister map of FB450 steel charged with arsenic-based electrolyte

		TIME										
		5 min	10 min	20 min	30 min	1 hour	2 hours	4 hours	8 hours	1 day	2 days	3 days
CURRENT DENSITY	50 mA/cm ²		X	X	X	X	X	X	X	X	X	X
	10 mA/cm ²							X	X	X	X	X
	5 mA/cm ²								X	X	X	X
	2 mA/cm ²											
	0.8 mA/cm ²											

The appearance of blisters on the sample surface is obviously influenced by the current density and charging time. As an illustration, figure 3 shows the micrographs of two charged samples of FB450 steel. In the sample charged for 5 minutes at 50mA/cm², the surface does not show blisters, while on the sample surface charged for 8 hours at 10mA/cm², blisters are visible on the surface.

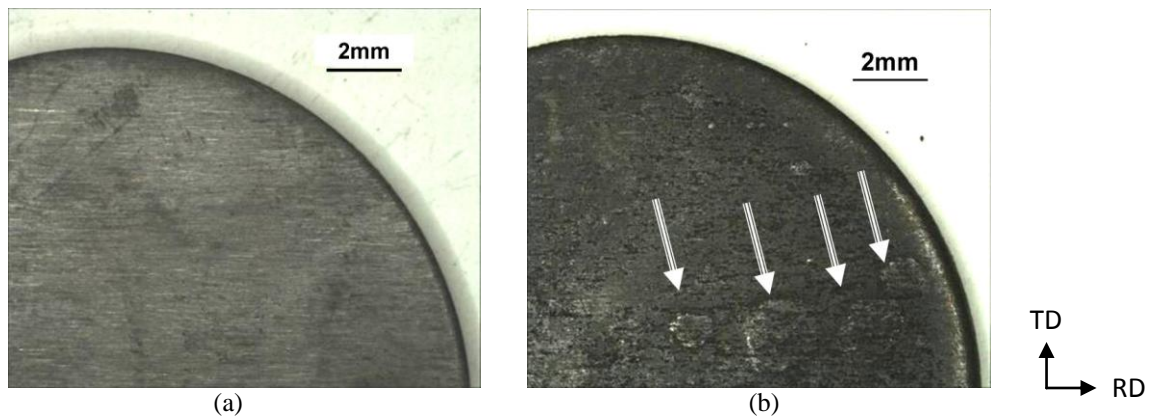


Figure 3. Stereographical microscopy of the FB450 after charging with the arsenic-based electrolyte. (a) 50mA/cm² for 5 minutes, (b) 10mA/cm² for 8 hours

Table 3 shows the results for the pure iron charged with arsenic-based electrolyte. It is clear that this material is more susceptible to damage during hydrogen charging.

It was found that for the samples charged with thiourea in NaOH the appearance of blisters started at higher current densities and longer charging times than those charged with the arsenic-based and thiourea in sulfuric acid electrolytes.

Evaluation of the microstructural damage by charging

Even though in some charging conditions, FB450 did not present blisters at the surface, the microstructure of the material was evaluated to check for other damage e.g. crack or voids. This was also done for the three other multiphase steels and pure iron. The materials were charged for 1 hour at $10\text{mA}/\text{cm}^2$, the surface present no blisters for all materials. Small or big cracks were identified in all materials, except for the S550MC. The cracks were situated in all the cases exactly in the middle of the sample and they propagate in the rolling direction as shown in Figure 4.

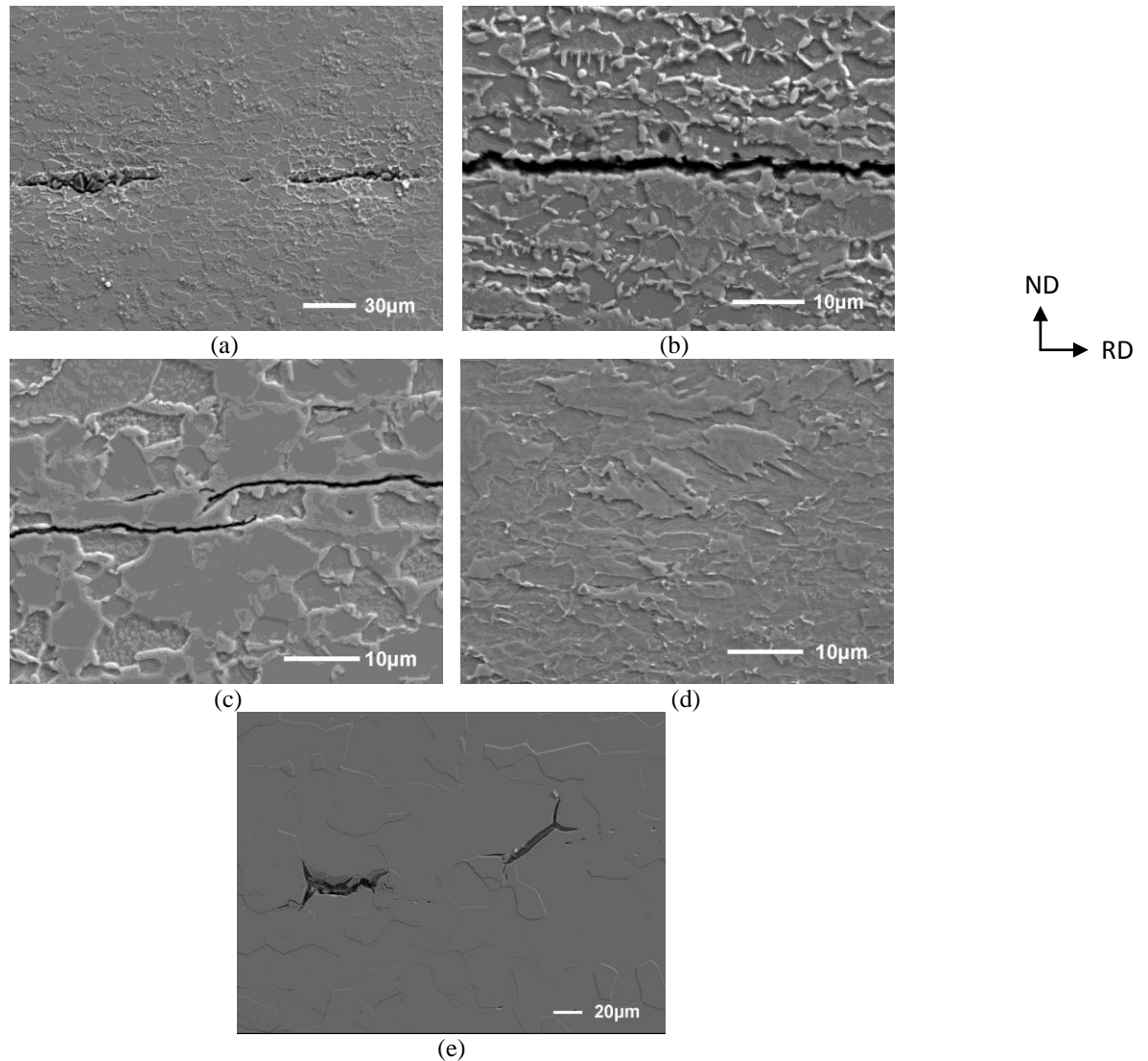


Figure 4. Scanning electron microscopy pictures of the multiphase steels after charging for 1h at $10\text{mA}/\text{cm}^2$
(a) FB450; (b) TRIP700; (c) DP600; (d) S550MC; (e) Pure iron

In order to search for an explanation for this observation, EDX mappings were performed. Figure 5 shows the results for the DP steel. The presence of manganese sulfides in the cracked regions was clearly demonstrated indicating their possible influence on the crack formation.

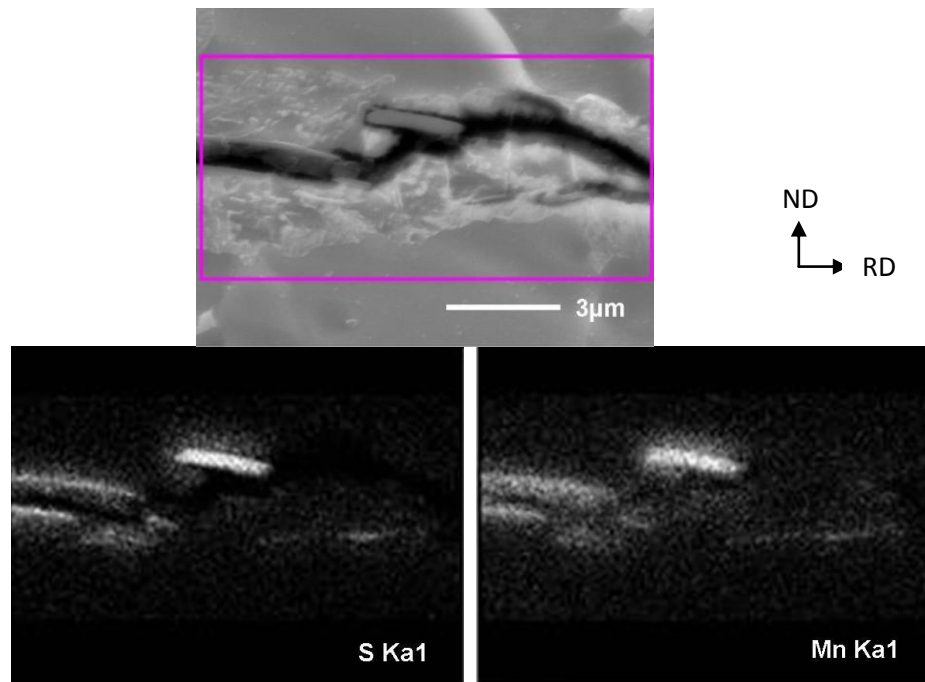


Figure 5. EDX mapping inside a DP600 crack

Wilde *et al.* [13] found that hydrogen-induced blister cracking, in H_2S environments, initiated at elongated manganese sulfide inclusions and glassy silicate inclusions or massive niobium carbonitride precipitates. Omizzi [14] investigated the influence of sulfur content and inclusion distribution on hydrogen-induced blister cracking in pressure vessel and pipeline steels and found that hydrogen induced cracking (HIC) could be correlated with the elongated MnS inclusion.

CONCLUSIONS

- Whenever a material is charged with H on laboratory scale, it should always be verified that the charging does not cause any damage on the material as this might influence further study of the sample.
- For any electrolyte used for galvanostatic charging, the blister formation enhances for higher current densities and higher charging times. Based on the blister map, a safe area of charging conditions can be defined where blisters will not occur.
- Blister formation was found to be dependent on the steel grade; *i.e.* pure iron was found to be more susceptible to hydrogen blister formation than a high strength ferrite bainite steel.
- Blister formation was found to be dependent on the electrolyte; for the same charging conditions the NaOH based electrolyte was found to cause less damage to the sample than the H_2SO_4 based solution.
- In the absence of blisters, cracks could sometimes still be observed in the samples. For the FB450, TRIP700 and DP600 they were situated in the centre of the sample. The S550MC did not show cracks when charged in the same conditions. Pure iron was found to be more susceptible to hydrogen internal damage than the high strength steels.
- Elongated MnS inclusions were found in the middle of the crack for the DP600.

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