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THE EFFECT OF HYDROGEN ON STEEL

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Abstract

Due to its small atomic size hydrogen can easily diffuse in steel, and interstitially incorporate in both α-, and γ solid solutions. It can appear in steel during steel production from excipients-, and additives (ex. limestone or ferrosilicon), during processing (ex. casting, welding, heat treatment) and during functioning of steel components. The purpose of this paper is to give an overview about the effect of hydrogen on the mechanical properties, and to identify hydrogen damage mechanisms in steel components.

1 Introduction

Because of the high number of industrially important – hydrogen-related – degradations that have occurred during the last decade, hydrogen damage of steel components has been investigated by many authors.

Hydrogen in iron-based alloys does not form metallic compounds or microstructures with the base element or with alloying elements. The solubility of hydrogen in iron increases with the temperature as shown in figure 1.

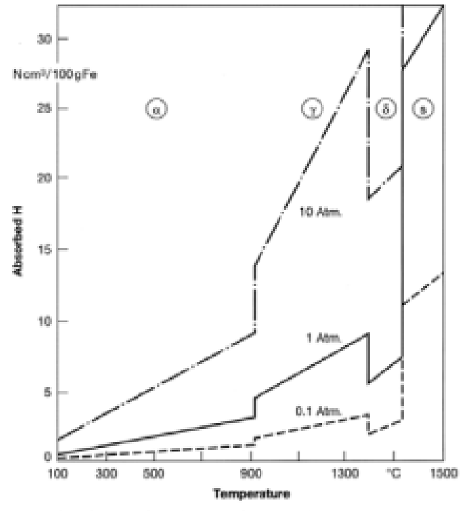

Figure 1. Solubility of hydrogen in iron in function of temperature and pressure (Woodtli, J., R. Kieselbach, 1999) [7]

The diffusivity of hydrogen in iron is high even at lower temperatures, so as, at a temperature of 100-150℃ at grain boundaries, lattice defects or micro-pores the hydrogen-atom density is high, it can form molecules. The diffusivity of the latter is low, thus the pressure in these inclusions can reach $10^2 \ldots 10^3$ MPa [6]. If the pressure exceeds the value of the tensile strength, the inclusions situated near the surface of the steel can open up and the surface of such steels appear flaky. Hydrogen induced flaky cracks can occur in other metallic materials as well.

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Due to the development of chemical industry, and the increasing number of hydrogenation equipment, the number of hydrogen induced damages at elevated temperatures increased. Carbon steels have low resistance against hydrogen at temperatures above 200℃. Hydrogen reacts with iron-carbide according to the following equation: $Fe_3C+2H_2 \rightarrow CH_4+3Fe$. This results in high internal stresses, and may cause the embrittlement of the steel and eventually the apparition of cracks. This process is accelerated by higher temperatures and/or pressures. In alloyed steels, where carbon forms carbides with strong carbide forming elements such as chromium, molybdenum, rather than with iron, hydrogen is not able to resolve the carbon. This is valid in the case of micro-alloyed steels with vanadium, titanium and niobium as well.

2 The effect of hydrogen on the toughness of steel

Gas transporting pipes in low temperature environment can behave in a brittle way, this behavior in the presence of H_2S and CO_2 can increase the risk of brittle failure caused by hydrogen embrittlement. Low alloy steel and carbon steel are commonly used in oil and gas industry. Therefore, experiments were carried out to determine the effect of hydrogen on ductile-brittle transition curves of these steels. Figure 2 shows the results of impact test of two medium strength low alloy steel in uncharged state and charged with hydrogen. The electrochemical hydrogen charging was carried out in such condition that could be compared to that found in pipeline steel after a long service time. The diffusible hydrogen content of the charged specimens were in the range of 0.6-2 ppm.

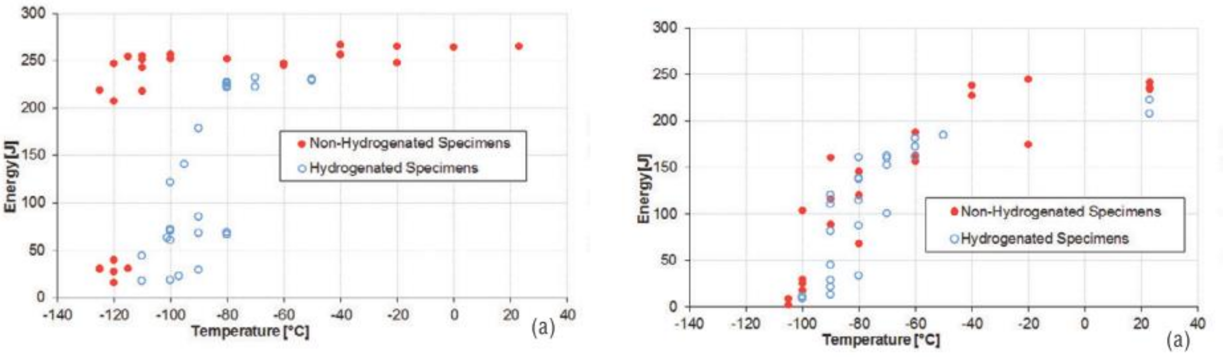


Figure 2. Impact energy of two steels at different temperatures [1]

The brittle tough transition temperature of the two steels is different. These diagrams indicate that in the presence of hydrogen in both cases a slight increase of the transition temperature was found, and the results are more scattered in the case of hydrogenated samples compared to uncharged material.

3 The effect of hydrogen on the steel's strength properties and ductility

Another research focused on the determination of the material embrittlement during long-term operation of the main gas pipelines by determining the strength properties of 17MnSi steel after 31, 38 years of operation and comparing with its initial state. From the complete stress-stain diagrams (Figure 3) of these materials can be concluded that the long-term operation results in the reduction of the material ductility. In the gas pipe the hydrogen is concentrated in the regions of strain localization resulting in reduced crack resistance manifested through the microdefect grows in the gas pipeline material wall, and reduction of its resistance to brittle fracture [5].

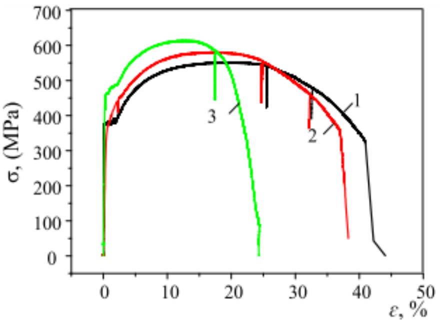


Figure 3. Stress-strain diagrams of 17MnSi steel specimens under static tension: 1 - as-received state, 2, 3 – specimens from pipelines from two different locations functioning 38 and 31 years [5]

The effect of hydrogen on tensile strength, ductility and fracture behavior of low alloy steels used for reactor pressure vessel in light water reactors was also investigated. The hydrogen absorbed from the high temperature water environment and corrosion reactions may reduce toughness of these steels in synergy with other embrittlement mechanisms like thermal aging or dynamic strain aging [3]. Figure 4 shows the values of ultimate tensile strength and reduction in area of two low alloy steels with different dynamic strain ageing susceptibilities with and without hydrogen at 288°C.

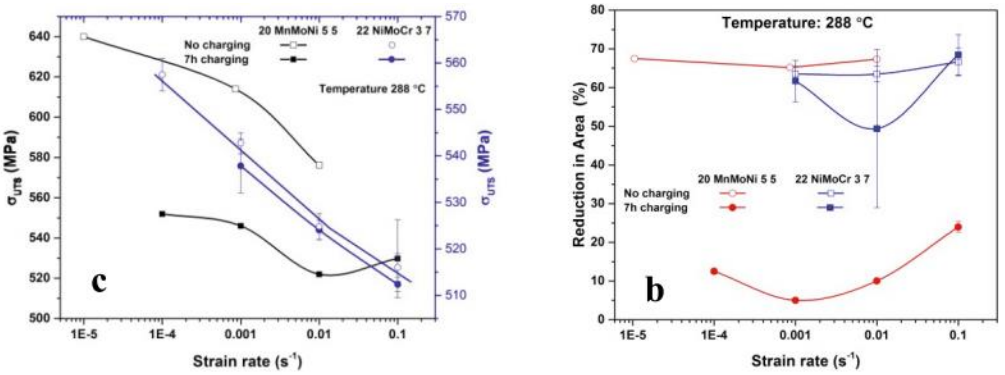


Figure 4. Ultimate tensile strength and reduction in area with and without hydrogen in two low alloy steel for different strain rates at 288°C [3]

Under identical hydrogen charging conditions, the reduction of ultimate tensile strength is higher than in steel with low dynamic strain ageing susceptibility and a maximum in softening was observed at strain rate of 0.01 s^{-1} in steel with high dynamic strain aging susceptibility with significant scatter in this region. From this can be concluded that the effect of hydrogen is significantly amplified by a high dynamic strain aging susceptibility in the dynamic strain aging temperature – strain range [3].

As fuel cell systems can be a potential next-generation energy system, the adaptation of the materials to the new demands for hydrogen storage and transport using higher hydrogen pressures up to 70 MPa must be solved. The use of medium and high strength steels can be economical, because it allows the use of pipes with lower thicknesses. Steels for hardening and high temperature tempering can offer good strength and toughness combination. For example two steels (42CrMo4 and 2.25Cr1Mo) where pre-charged with gaseous hydrogen in a high-pressure reactor, and tensile tests were carried out on smooth and notched specimens. The results showed that smooth specimens are not suitable to evaluate hydrogen embrittlement, but in the surrounding of sharp notches the deleterious effect of hydrogen are better seen and the lowest rates of load application gave rise to highest embrittlement indexes due to the fact that hydrogen atoms have more time to diffuse and attain the process zone [4].

Hydrogen can enter into the steel components during surface treatment technologies such as pickling the surface of mild steel in strong acids before coating. This is a critical step of the coating process, therefore researches focused on adding different types of adsorption inhibitors to the pickling bath to prevent metal dissolution and related hydrogen evolution, and determining their effect on mechanical properties. As an example retaining rings for shafts where examined by subjecting to cyclic fatigue test in as-received state and after pickling in the acid solutions without and with inhibitors (Urothropine – contains nitrogen atoms, hexamethylenetetramine – A: contains oxygen atoms, B: polymer with repeating NH group and C: A + a complex forming agent) [8]. Results are shown in Figure 5.

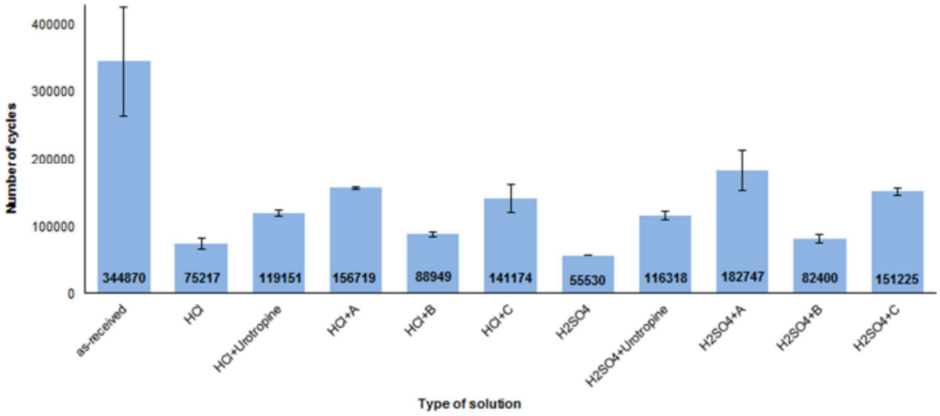


Figure 5. Total number of cycles measured for the retaining ring tested as-received and exposed to acid solutions with and without inhibitors [8]

From this figure it can be concluded that the use of inhibitors significantly increased the number of cycles which the samples withstand in comparison with samples pretreated in pure acids. The results also show that the effect of inhibitor does not depend on the acid type it was mixed with. [8].

4 Hydrogen induced degradation and damage mechanisms in steels

In many cases mechanical testing is followed by fractographic examinations, where according to the failure types the morphology of the fractured surfaces can show evidence of the hydrogen induced cracking.

In presence of hydrogen the fractured surface after tensile test showed shear dominated mixed mode with varying amounts of ductile microvoid coalescence, quasi-cleavage regions and secondary cracking confirming the role of hydrogen-induced micro-plasticity [3] (figure 6.).

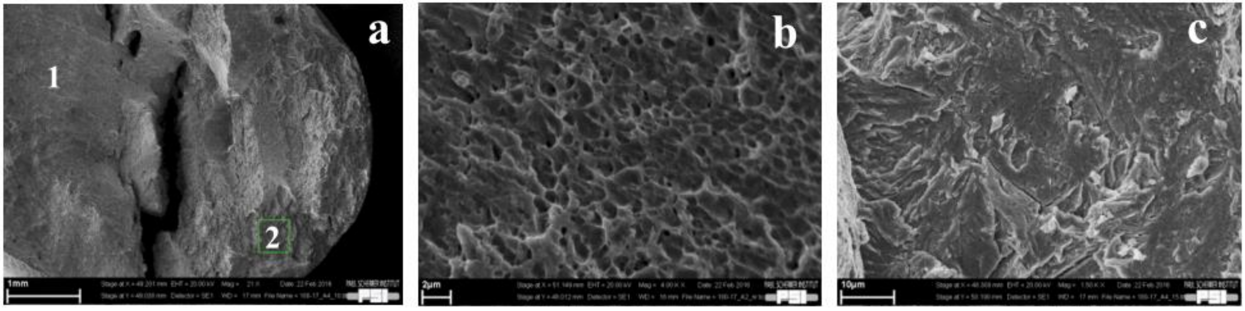
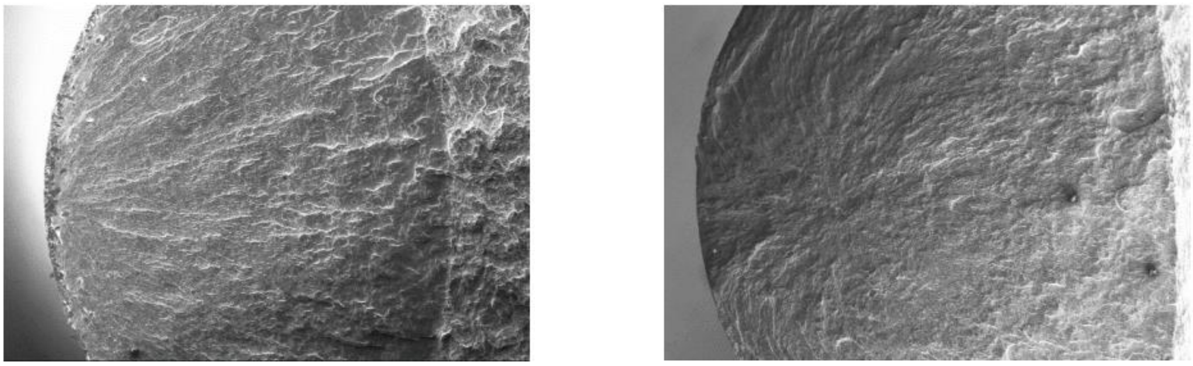


Figure 6. Fracture morphology after hydrogen charging in 20MnMoNi5 5 tested at 288°C and strain rate of 10^{-2} s^{-1}: a) overall fracture surface, b) magnified view of region 1, c, d) magnified view of region 2 [3]

Fatigue testing is considered to be most suitable to reveal the presence of the hydrogen and its negative effect in steel. In Figure 7 significant difference is observed between the crack initiation in the case of fatigue failure of uncharged and hydrogen charged low-strength Cr-Ni-Mo-V steel used as a steam turbine rotor material: specimen surface crack initiation for as-received specimens (Figure 7.a), while interior micro-defect for hydrogen charged specimens (Figure 7.b) In Figure 7.b a fish-eye pattern is observed and an inclusion is found at the center [9].



a) b)

Figure 7 a) as-received specimen, b) hydrogen charged specimen [9]

It seems that several inclusions have been activated as potential crack initiation sites for hydrogen charged specimens, indicating the hydrogen element tended to be trapped by micro-defects.

5 Conclusions

- The presence of the hydrogen in steels affects their mechanical properties causing embrittlement of the steel.
- Care should be taken for continuous monitoring the behavior of steels functioning in hydrogenating media in order to avoid the accumulation of damages caused by other different influencing factors such as temperature, stress state, environmental corrosion as well.
- There is an increased need to work out methods and technologies to impede the diffusion of the hydrogen in steels that are functioning in gaseous or other aggressive media.
- Applying hydrogen contamination barriers or inhibitors can be a solution to decrease the number of damages caused by hydrogen.

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