Corrosion Science 54 (2012) 106–118

Contents lists available at SciVerse ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Hydrogen trapping in an API 5L X60 steel

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ARTICLE INFO

Article history:
Received 21 May 2011
Accepted 9 September 2011
Available online 16 September 2011

Keywords:
A. Steel
B. Hydrogen permeation
B. Modelling studies
C. Effects of strain

ABSTRACT

Electrochemical hydrogen permeation tests were performed on an API 5L X60 steel to study trapping and diffusion properties in the as-received (AR) and in a cold-rolled (CR) state, at 30, 50 and 70 °C. Hydrogen trapping was characterized by assuming saturable traps in local equilibrium. Binding energies (ΔG) and trap densities (N) were determined by fitting a trapping theoretical model to experimental data. Both conditions AR and CR present a high density of weak traps $|\Delta G| < 35$ kJ/mol, namely $N = 1.4 \times 10^{-5}$ and 7.9×10^{-4} mol/cm^3 respectively. Strong trapping sites were detected ($-72 < \Delta G < -57$ kJ/mol) and their densities increased markedly after cold-rolling.

1. Introduction

The steels specified in the API standard (American Petroleum Institute), are mainly used in natural gas and petroleum pipelines, and are generally characterized by their good mechanical strength, weldability and fracture toughness among other properties [1]. However, these materials are susceptible to some type of hydrogen damage. A well known type of damage is the hydrogen assisted cracking. This phenomenon, which has been studied extensively [2–5] is related to hydrogen diffusion. Ferritic and martensitic steels have microstructural imperfections called traps which hold hydrogen in the atomic form. A remarkable observation is that the H diffusion process is delayed by the presence of traps. These traps have been related to microstructural features such as dislocations, interfaces, vacancies, impurity atoms, microvoids or any other lattice defect [4]. The effect of cold-working on the hydrogen trapping characteristics of iron and steels has been studied extensively; the pioneering works appeared in the 1950’s. Darken and Smith [6] suggested that in steels subjected to a cold-rolling process, the H diffusion can be affected by the presence of traps which are created during the plastic deformation of the material. Bath and Lloyd [7] studied different steels (with different carbon percentage), which were cold-drawn to different reduction degrees. The experimental setup was a hollow steel cylinder in which hydrogen was introduced by cathodic charging on the external surface. After permeating through the steel wall, hydrogen was collected in the internal hole and measured by a volumetric method. Their results indicated that the H permeation rate at room temperature increases with time and finally reached a steady state value. The time to reach the steady state increased markedly as the degree of plastic deformation increased. They observed also that the steady state permeation rate decreased markedly with increasing plastic deformation. However, they were suspicious on the latter result and argued that either the different rates of hydrogen pickup (cathodic charging) or insufficient time to attain a true steady state might have influenced the results. In fact, later results [8] showed a moderate influence of the degree of cold-work on the steady state H permeation rate in a 0.48%C steel. In additional experiments [7], the amount of hydrogen absorbed after 24 h cathodic charging (“H saturation”) was measured by hot extraction in vacuum. Bath and Lloyd [7] observed that the H saturation became is higher as the degree of cold-work increased. This confirmed the hypothesis that plastic strain created sites that capture hydrogen. In other classical work Keeler and Davis [9] showed, *via* H_2-equilibration with a Sieverts-like technique, that the amount of H absorbed by a SAE 1020 steel (0.17 %C) at 250–550 °C steel was influenced by a cold-rolling process performed on this material. Thus, the amount of H occluded in the plastically strained steel after equilibration at 250 °C was about 100 times higher than the amount of H occluded in the not strained steel. Keeler and Davis [9] also observed that the density of the 1020 steel decreased as the degree of cold-work increased up to 60% reduction in thickness. They attributed the decrease in density to the formation of microvoids as result from imperfect plastic flow of the ferrite about inclusions or other phases during cold-rolling. The increase in the hydrogen absorption capacity was related to these microvoids. However, additionally to the microvoids, they proposed a second type of trap which was eliminated by annealing.

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0010-938X/$ - see front matter
doi:10.1016/j.corsci.2011.09.008

Numerous works along a period of six decades dealt with the creation of hydrogen traps in iron and iron base alloys as a result of plastic deformation. Just a selected group of papers concerning the behavior of hydrogen in pure iron or low alloy steels is cited here. The most frequently applied techniques were hydrogen permeation [10–12] and thermal desorption spectroscopy [13,14]. As a result of these investigations, different microstructural defects in the deformed material have been associated with hydrogen traps. Dislocations are naturally the first candidates [12–14]; however, the density of hydrogen traps calculated from the density of dislocations is not equal to the trap density inferred from permeation measurements [10]; moreover, trap density decreases markedly after annealing at low temperatures at which the dislocations should be stable [10]. Microvoids caused by cold-work are other possible type of traps [9,10,13]. However, the results of permeation tests are not consistent with this type of non-saturable traps [15]. Nagumo et al. [14] proposed that vacancy clusters produced by cold-work are important hydrogen traps. In the case of low alloy steels, additional trap types such as interfaces with second phase particles are considered [12]. With reference to the hydrogen exchange rate between trap sites and normal interstitial lattice sites (NILS), usually the local equilibrium hypothesis [16] is assumed. This implies a high NILS-trap exchange rate in comparison with the diffusion rate. However, thermal desorption results are better described as limited by an activated release rate from the traps [13]. This brief literature review is intended to show that there is still a controversy on the true nature of the hydrogen traps in deformed iron and steel, and on the way these traps exchange hydrogen with NILS.

As result of the delay in the H diffusion because of the presence of lattice imperfections, the apparent diffusion coefficient (D_{app}) is lower than the diffusion coefficient in a perfect body centered cubic lattice of iron (D_L). The magnitude of the H diffusion delay depends on the strength of the trap, i.e. the free energy of trapping (ΔG) and the trap density (N), i.e. the number of trap sites per unit volume. Both parameters, ΔG and N, can be calculated through the theoretical fit of experimental H permeation curves of the H flux J_H [mol H/(cm^2 s)] versus time t [s]. In the present work, i_H vs. t curves were obtained from H permeation tests with electrochemical detection, i_H [A/cm^2] being the current density due to the oxidation of H at the exit side of the permeation membrane, i.e. the faradic equivalent of J_H. In the present work, a numerical method has been used to calculate theoretical permeation transients. This method, which is described in the Appendix, solves the differential equations described in the McNabb and Foster work [17]. These authors assume the presence of one type of trapping site and they define two kinetic constants for the H trapping and H release named k and p respectively. Also, they consider that traps are saturable, i.e. each trap can retain only one H atom; in this way the H saturation concentration is equal to the density of traps. In 1970, Oriani [16] simplified the model proposed by McNabb and Foster, assuming that the trapping and liberation velocities are high enough in comparison with the velocities involved in the diffusion process. This implies a local equilibrium condition between H in traps with the diffusing H. The numerical resolution for the MacNabb and Foster diffusion equations has been developed for several authors [15,18,19]. In these literature works, the permeation transients were numerically simulated by fixing the values of the parameters D, k, p and N, where D is the diffusion coefficient. Johnson and Lin [15] simulated the H permeation transients to study the nature of traps in cold-rolled iron. Ramunni et al. [19] obtained the trapping parameters for three different morphologies of the cementite Fe_3C, generated by an adequate scheme of thermal treatments.

In the present work the diffusion and trapping parameters of an API 5L X60 steel were obtained from the data of hydrogen permeation experiments with gas phase charging and electrochemical detection. Two different sample conditions were studied: as-received from the manufacturer (AR), and cold- rolled with a thickness reduction of *ca.* 2% (CR). The H trapping energy (ΔG) and the trap density (N) of the API 5L X60 steel were calculated from the H permeation data based on the theoretical considerations described in the Appendix of the present work, under the assumption of saturable traps in local equilibrium. As shown in Section A.7 of the Appendix, trapping energy values in the range of -35 to -70 kJ mol^{-1} are considered as "strong" or high energy traps, and their particular N and ΔG values have been directly assessed from the permeation data as fitting parameters; traps with $|\Delta G| \leqslant 35$ kJ mol^{-1} are considered as "weak" and their effect is only reflected in the value of the apparent diffusion coefficient D_{app}, which is reduced in comparison with the diffusion coefficient of a trap free lattice of bcc iron D_L.

2. Materials and methods

The material employed in this study is an API 5L X60 steel taken from a seamless pipe. The chemical composition is shown in Table 1.

A previous work [20] reported the microstructural characterization and the study of the non-metallic inclusions of this material in the as-received (AR) condition. The metallographic observation indicated that the microstructure of the API 5L X60 contains equiaxed ferrite grains and carbides mainly located in the grain boundaries, which is typical of tempered martensite. The average grain size is estimated as 4 μm and the mean size of the observed cementite particles is *ca.* 0.3 μm. Analysis of the local chemical composition by Energy Dispersive X-ray Spectroscopy microanalysis (EDAX) revealed few non-metallic inclusions containing varying amounts of Ca, S, Al and Ti.

From this material a parallelepiped of *ca.* 3.5 mm thickness was constructed, which was subjected to plastic deformation by cold-rolling in consecutive steps. The reduction in thickness (e) was 2.1 ± 0.3%, and it was calculated according to:

$$e = (L_i - L_f)/L_i \quad (1)$$

where L_i is the parallelepiped thickness before cold-rolling and L_f is the parallelepiped thickness after the last step of rolling. From the rolled parallelepiped a disk was made with a thickness of 3.39 mm and a diameter of 35 mm. Also, a disk with a thickness of 1.57 mm and a diameter of 35 mm was cut directly from the AR material. These disks were used in the electrochemical permeation tests as the permeation membranes representative of the CR and AR conditions, respectively. Prior to the tests, both disk faces (entry and exit surface of the permeation membrane) were ground with SiC up to #600 grit and then electropolished in a mixture of 10% $HClO_4$ and 90% butyl cellosolve at a temperature below 5 °C under a potential difference of 36 V. The objective of electropolishing is to eliminate a layer of 10 μm of material from each membrane face, which is the estimated thickness of the deformed layer created by mechanical polishing. Then, a palladium film about 10 nm thick was electrochemically deposited on both membrane entry and exit surfaces. The deposition cell was equipped with a Pd/PdH reference electrode and a Pt counter electrode, and it was filled with *ca.* 300 ml of electrolyte, which was an aqueous solution of 0.1 M NaOH. The electrolyte was continuously deaereated by nitrogen bubbling. Prior to the deposition, the permeation membrane was etched in HCl 50%, rinsed with water and immediately subjected to cathodic polarization in the electrochemical cell at a constant current density of -0.1 mA cm^{-2}. The cathodic treatment continued until the typical potential of H_2 evolution on the steel (-0.970 mV vs. normal hydrogen electrode, NHE) was reached. The deposition was started by introducing in the cell 7 ml of an aqueous solution of $[Pd(NO_2)_4]Na_2$