

Hydrogen Charging of Armco iron and L80 steel in various Electrolytes

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ABSTRACT

Abstract

Armco iron and L80 steel (according to API 5CT) were charged under various conditions due to the lack of knowledge of the amount of hydrogen, which is absorbed during operation and laboratory charging. These two materials were charged in sodium chloride (NaCl), sulfuric acid (H₂SO₄), both with and without addition of thiourea (CH₄N₂S) and in H₂S (NACE TM0177) at open circuit potential.

Additionally, cathodic charging was done in sodium chloride and sulfuric acid, both with thiourea added at a current density of 1 mA/cm². The charging time was between 2 and 200 hours for both methods.

Most of the immersion tests at open circuit potential resulted in hydrogen concentrations of up to 1 wt. ppm, while cathodic loading led to values of up to 4 wt. ppm. In addition, the NACE TM0177 test provided the highest hydrogen concentrations and was the only test to show higher hydrogen concentrations for the Armco iron than for the L80 steel.

Key words: Hydrogen, Materials Performance, Hydrogen Embrittlement, Hydrogen Induced Cracking

INTRODUCTION

Facing the increasing industrial requirements on iron and steel products the importance of investigating hydrogen embrittlement has been rising straightly since *Johnson* first described the influence of hydrogen on the mechanical properties of iron and steel in 1874¹. Since this day a lot of effort has been done on understanding and describing the mechanism of hydrogen embrittlement and how absorbed hydrogen performs in materials.

This work aims in providing a deeper knowledge about the processes of hydrogen uptake in iron and steel in general and to determine the hydrogen uptake of L80 steel and Armco iron under various conditions. Beside the uptake also the desorption of hydrogen from L80 steel and Armco iron was investigated.

For the absorption into solid metals hydrogen is required to be in atomic form due to its diffusibility. The atomic hydrogen is adsorbed at the interface of metal and the surrounding media from where it is absorbed into the bulk material. Absorption can take place in three different ways.

The first possibility is the hydrogen uptake out of a gaseous atmosphere where the hydrogen partial pressure is of crucial importance for the achieved hydrogen content. This is due to Sieverts law given in the following equation:²

$$c_H = K_S \times \sqrt{p_{H_2}} \quad (1)$$

Where c_H is the concentration of dissolved hydrogen, K_S the Sieverts constant and p_{H_2} the hydrogen partial pressure. In order to this an increase in partial pressure leads to higher concentrations in the material. Apart from partial pressure the hydrogen concentration can be influenced mainly by the temperature where high temperatures accelerate dissociation processes and increase the hydrogen concentration in the material. For pressurized hydrogen charging Nelson curves show resistance limits of materials as a function of partial pressure and temperature.³

Corrosion reactions in aqueous media are a second way for hydrogen uptake which takes place in several sub steps and can be investigated by performing immersion tests.

In acidic solutions the first step is the transport of a hydronium ion to the metal/solution interface where it is reduced to atomic hydrogen following the Volmer reaction, given in the following equation:⁴⁻⁶



Hydrogen atoms formed due to Volmer reaction are adsorbed at the metal surface and can either be absorbed (3) or recombine to H_2 molecules which desorb from the surface following the Tafel reaction (4). Beside the Tafel reaction another mechanism according to Heyrovsky (5) and (6) is known for the recombination and desorption of hydrogen.⁵



Usually the hydrogen activity throughout these electrochemical reactions is low, because of the high reaction rate the recombination reaction has compared to the formation reaction. Due to the fact that the amount of adsorbed hydrogen atoms at the surface is in equilibrium with the amount dissolved in the metal the hydrogen uptake under normal conditions (low hydrogen activity) is expected to be low. Therefore the hydrogen uptake during immersion tests depends strongly on the corrosion attack, because an increasing corrosion attack results in a higher formation of hydrogen atoms which adsorb at the materials surface and can be absorbed.

Beside the corrosion attack also the presence of hydrogen recombination poisons as well as the materials microstructure are important influences on the hydrogen uptake in electrolytic hydrogen charging. The most common recombination poisons are arsenic oxide, hydrogen sulfide, ammonium thiocyanate and thiourea. Although the mechanisms are different for all hydrogen recombination poisons their addition result in inhibiting the recombination reaction of adsorbed hydrogen atoms and thus increases the hydrogen absorption into the material.^{7–10} Apart from its function as recombination poison thiourea also acts as corrosion inhibitor which reduces the corrosion attack¹¹.

Cathodic hydrogen charging is the third option how materials can be charged with hydrogen^{12; 13}. By applying a potential, the material which should be charged is cathodically polarized and atomic hydrogen is formed by reducing the hydrogen contained in water molecules according to equation:¹⁴



The current density applied to charge the sample is the most important parameter in cathodic hydrogen charging. Also the choice of the charging solution (acidic or neutral) is influencing the charging process due to the additional hydrogen formation by corrosion reactions when using acidic solutions.¹⁵

EXPERIMENTAL PROCEDURE

Materials Investigated

For the investigations cuboid samples of L80 steel (API⁽¹⁾ 5CT L80 Type 1) and Armco iron were used. The specimen geometry was 30 x 6 x 6 mm (1.18 x 0.24 x 0.24 in) for all tests with as machined surface condition. Armco iron used for samples was in annealed condition. The annealing process contains of a one-hour diffusion annealing done in stainless steel foil to inhibit scaling of the material followed by air cooling. L80 steel samples were fabricated out of a commercially available seamless tube. The designation L80 indicates the minimum yield strength of the steel, which is 80 ksi (corresponding to 552 MPa). The chemical compositions of the two investigated materials are given in Table 1.

Table 1: Chemical compositions of Armco iron and L80 steel

Material	C [wt%]	Mn [wt%]	Si [wt%]	P [wt%]	S [wt%]	Cr [wt%]
Armco iron	0.004	0.05	0.01	0.005	0.000	0.03
L80 steel	0.33	1.38	0.21	0.017	0.009	0.25

In figure 1 the microstructures of both investigated materials are documented. The microstructure of the tested Armco iron consists of large ferrite grains with a grain size in the range of 100 µm. There are no evidences for a second phase or precipitates. In comparison to the structure of Armco iron the microstructure of L80 is much finer which indicates a higher number of traps. L80 steel has a microstructure consisting of tempered martensite with a former austenite grain size between 20 and 40 µm.

⁽¹⁾ American Petroleum Institute (API), 1220 L St., N.W., Washington, DC 20005-4070.

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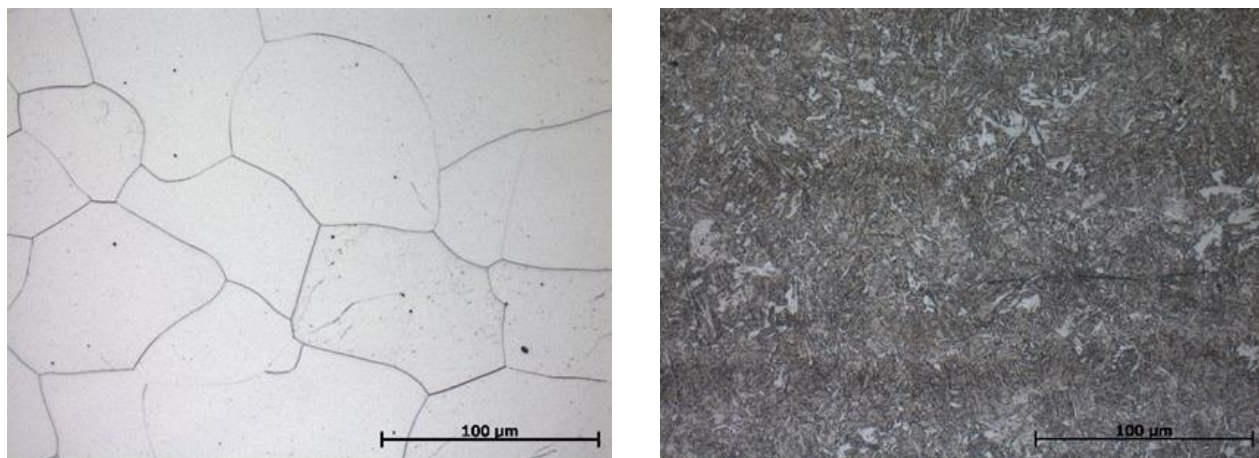


Figure 1: Microstructure of the examined materials: Armco iron (left) and L80 steel (right)

Table 2 shows the mechanical properties of the tested materials.

Table 2: Values of the measured Hardness and the estimated Ultimate Tensile Stress (UTS) of the investigated materials

Material	Hardness	UTS	
	HV 1	[MPa]	[ksi]
Armco iron	88	255	37
L80 steel	247	780	113

Testing Method

Before performing charging tests under various conditions (details see Table 3) the bulk hydrogen content of L80 Steel and Armco iron was determined by hot carrier gas extraction at 950 °C (1742 °F).

Immersion tests were performed in a beaker filled with 600 ml of test solution which corresponds to a ratio of sample surface area to the volume of test solution of 76 ml/cm². Two different electrolytes were used, the first was a 3.5 % NaCl solution and the second one was a 1 m H₂SO₄, both with and without an addition of 1 g/l thiourea. The investigations were performed at 298 K and testing time was varied from 2 to 200 hours. To prevent evaporation during long test periods the beaker was covered with a sealing film.

Cathodic charging experiments were performed by using 3.5 % NaCl and 1 m H₂SO₄ with an addition of 1 g/l thiourea as electrolytes. To provide homogeneous charging conditions throughout the whole sample the specimens were placed in the center of a cylindrical platinum mesh electrode during cathodic charging. For avoiding local changes of the test solution due to electrochemical reactions a magnetic stirrer was used during charging. A PeakTech 6225A Power Supply[†] was used as voltage source to vary the charging current between 1 and 10 mA/cm².

During charging in sour gas atmosphere, the samples were placed on the bottom of a glass container which was subsequently filled with test solution and test gas (according to NACE TM0177).

The pressurized hydrogen charging was performed at 298 K in autoclaves with a test volume of 185 ml. All autoclave tests were performed with dry H₂ gas.

Independently from the applied test method, the following general procedure was carried out:

1. Every sample has to be cleaned and degreased in an ultrasonic bath for 3 minutes, in used acetone followed subsequently by a cleaning step with fresh acetone;
2. Drying off the acetone;

[†] Trade name

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