Corrosion Science 67 (2013) 184–192

Contents lists available at SciVerse ScienceDirect

Corrosion Science

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

The effect of the partial pressure of H_2S on the permeation of hydrogen in low carbon pipeline steel

Chengshuang Zhou, Shuqi Zheng *, Changfeng Chen, Guiwu Lu

Department of Materials Science and Engineering, China University of Petroleum, Beijing 102249, China

ARTICLE INFO

Article history:
Received 9 July 2012
Accepted 21 October 2012
Available online 27 October 2012

Keywords:
A. Carbon steel
B. Hydrogen permeation
B. Hydrogen embrittlement
C. Reactor conditions
C. Acid corrosion

ABSTRACT

The effect of different partial pressures of H_2S (P_{H_2S}) on the hydrogen permeation behaviour of API-X52 pipeline carbon steel was investigated in a high-temperature and high-pressure hydrogen permeation device. The results showed that the peak value of the hydrogen permeation curves, the corrosion rates, the susceptibility to hydrogen induced cracking and the amount of diffusible hydrogen significantly increased with increasing P_{H_2S}. Hydrogen permeation rate was affected by both P_{H_2S} and corrosion product films. The dense and incrassated corrosion product films provided significant protective properties and suppressed the production of hydrogen atoms.

1. Introduction

As an increasing number of sour oil and gas fields containing H_2S have been actively exploited in recent years, the application of pipeline steel has been limited because of mechanical and corrosion problems induced by hydrogen. Hydrogen damage is one of the major causes of steel equipment failures in the oil and gas industry [1–4]. Hydrogen-induced cracking (HIC) [5–7] refers to internal cracks that are generated by the recombination of hydrogen atoms to form gaseous molecules at certain appropriate traps in the steel, such as manganese sulphide (MnS) inclusions or pearlite bands, and sulphide stress cracking (SSC) [8–10], which is generated from the surface of the steel and requires an applied stress, are major problems for pipeline steels during service in environments containing H_2S. The diffusion of atomic hydrogen into the steel is the first step not only for HIC but also for SSC when in the presence of hydrogen sulphide gas (H_2S) in acidic solutions or hydrogen sulphide ions (HS^-) in neutral and alkali solutions, which reduces the rate of hydrogen gas formation on the steel surface [11,12]. Therefore, hydrogen permeation studies are important for researching hydrogen damage and for safety during production in oil industries [13].

Hydrogen permeation through a metallic membrane by an electrochemical technique is a widely used method for studying hydrogen diffusivity and metallic embrittlement phenomenon [14–25]. Hydrogen permeation measurements have long been used for assessing the hydrogen cracking mechanisms of steels by determining the hydrogen concentration and diffusion properties [26–33]. The environmental factors that critically affect the hydrogen permeation are considered to be the pH and H_2S partial pressure (P_{H_2S}) in the in-service environments because both the pH and P_{H_2S} affect the diffusion of hydrogen atoms in steels [30,32–34]. These authors observed that above a certain H_2S partial pressure, the steel corrosion rate decreased, thereby resulting in a decrease of the permeation rate. This decrease might likely be explained by the build-up of an iron sulphide layer, a reduced corrosion rate and a hydrogen reduction reaction. However, the authors did not provide strong evidence, and unfortunately, all the tests were performed under a P_{H_2S} that was less than 1 atmosphere; therefore, very little data are available for higher P_{H_2S}. As far as we know, there are a few essays concerning hydrogen permeation measurements in full-scale simulation tests at a P_{H_2S} of 1.5 MPa [35]. It is well known that the corrosion products that change over the H_2S concentration can promote or inhibit the iron corrosion, resulting in the formation of a ferrous sulphide (FeS) protective film on the electrode surface [36–38]. However, these reports also did not supply sufficient evidence. Therefore, it is necessary to perform additional work to study the hydrogen permeation in high P_{H_2S} environments.

The aim of the present investigation is to understand the effects of the H_2S partial pressure on the permeation of hydrogen in pipeline steels. To achieve this objective, a high temperature and high pressure electrochemical permeation cell was developed. The hydrogen permeation current was measured and compared in hydrogen sulphide solutions with different partial pressures of hydrogen sulphide. The corrosion rate and the amount of diffusible hydrogen were measured simultaneously. The corrosion product

* Corresponding author. Tel.: +86 10 89733200.
E-mail address: zhengsq09@163.com (S. Zheng).

0010-938X/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2012.10.016

was characterised using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental procedures

2.1. Tested material

The steel plates, which were X52 grade according to the API 5L specification, were used as specimens; these specimens were obtained from commercial products of API X52 grade pipeline steel. The chemical composition of the specimens, in wt% (all concentrations throughout this paper are expressed in wt%), was 0.13% C, 1.57% Mn, 0.46% Si, 0.012% S, 0.014% P and balanced Fe. The specimens were heated in the temperature range of 920–950 °C, followed by air-cooling. This heating resulted in the formation of a ferrite (F)/pearlite (p) microstructure, as illustrated in Fig. 1.

The specimens used for the permeation experiments were 25-mm-diameter plates with a thickness of 3 mm. All faces of the plates were machined to obtain a finish that was equivalent to that achieved using 1200-grit silicon carbide (SiC) paper. Specimens for the weight loss tests (sized $50 \times 10 \times 3$ mm) were pre-treated in a manner that was similar to the permeation specimens. The specimens used for measuring the amount of diffusible hydrogen were 40×40 mm plates with a thickness of 10 mm. The surfaces of these specimens were finished in the same manner as the permeation specimens.

2.2. Test solutions and exposure conditions

To clarify the effect of H_2S on the hydrogen permeation rate, all of the tests were performed in 5 wt% NaCl (the concentration of NaCl throughout this paper are expressed in wt%), and acetic acid was not applied to prevent the introduction of additional hydrogen ions. In this test, the influence of the P_{H_2S} was investigated as the major parameter; therefore, two levels of P_{H_2S}, 0.1 and 1.0 MPa, were selected. The temperature was 25 °C.

2.3. Electrochemical hydrogen permeation test

To investigate the effect of the high partial pressure on the hydrogen permeation, a high-temperature and high-pressure hydrogen permeation device was designed and manufactured, as shown in Fig. 2. In this device, the material to be tested is used as a bipolar electrode, which divides the device into two compartments: a hydrogen-generating cell (input side) and a hydrogen-oxidising cell (detection side). The material was sealed along with the hydrogen-generating cell with some insulating materials to allow them to remain sealed under more than 2 MPa of pressure. In the cathodic side, the cell is filled with test solutions, including a certain pressure of H_2S, and a potential is not applied. However, the detection side is filled with a 0.2 N NaOH solution, and an overvoltage of 250 mV_{SCE} is applied to oxidise the diffused hydrogen. The detection side of the steel membrane was electroplated with palladium (Pd) to eliminate flux-limiting surface impedances and to ensure the reliability of the hydrogen oxidation current. The thickness of the specimens is 3 mm to ensure that the specimens can withstand the 2 MPa of pressure. The hydrogen permeation rate (HPR) was determined from the hydrogen oxidation current density.

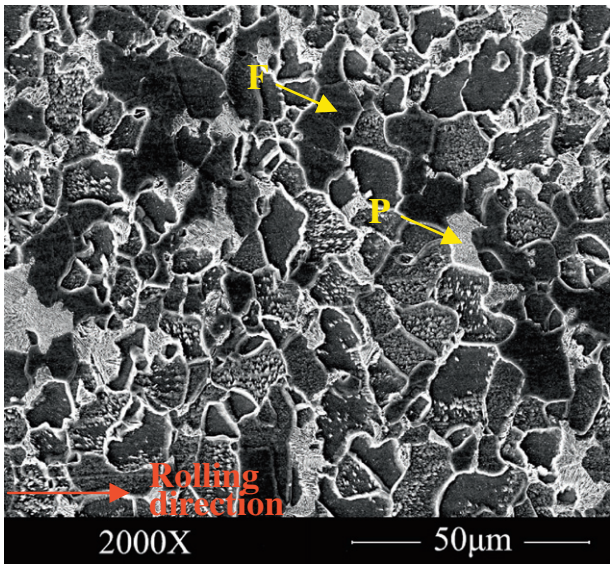

Fig. 1. Typical microstructure of X52 pipeline steels.

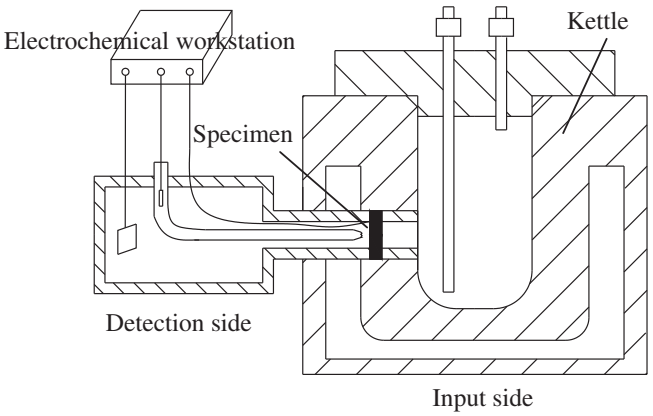

Fig. 2. Schematic for high-temperature and high-pressure hydrogen permeation device.

As the goal of the paper is to investigate the effect of H_2S partial pressure on the permeation of hydrogen in pipeline steels, the hydrogen is introduced into the samples by corrosion reaction of H_2S and iron instead of electrochemical charging. Thus, it is necessary to describe detailed procedures on permeation test. First, the specimen was clipped into the device. Next, the de-aerated 5% NaCl and the de-aerated 0.2 N NaOH were selected as test solutions in the hydrogen charging cell and the hydrogen oxidation cell, respectively. To ensure the continuous deaeration of the NaOH solution and NaCl solution in the passivated medium, N_2 gas was bubbled through the solution for 24 hr at a flow rate of 10 ml min^{-1} per litre of solution. Then, the potential of the steel membrane on the hydrogen oxidation cell was maintained at a potential of 250 mV_{SCE}, at which the dominant oxidation reaction was oxidation of hydrogen that diffused through the steel membrane. After 24 hr of passivating, the background current was stabilised and remained lower than 2×10^{-6} A (because the hydrogen charging cell was made of metal, so the background current was often higher than that from a cell made of an insulator whose background current can often be lower than 0.5×10^{-6} A), the N_2 gas was stopped and H_2S gas was continuously bubbled through the 5% NaCl solution and maintained a requirement of a partial pressure (inaccuracy 0.05 MPa for 1.0 MPa of H_2S) and a controlled flow rate of 10 ml min^{-1} per litre of solution to ensure fresh H_2S gas. The hydrogen oxidation current was continuously measured.

The apparent hydrogen diffusivity in steels can be determined using the breakthrough time method or the relaxation time method [39]. In this study, the relaxation time method was used to determine the hydrogen diffusivity for the tested steels.