Short Communication

Development of a hydrogen absorption model to determine absorption kinetics and diffusion coefficients by means of carrier gas hot extraction

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ABSTRACT

Precise description of the hydrogen charged state of mechanical test specimens including the spatial and energetic hydrogen distribution is considered to be essential for understanding the mechanisms of hydrogen embrittlement. Here, a simple hydrogen absorption model for hydrogen charging in liquids was developed for cylindrical specimens. The absorption model is based on an approximate solution of Fick's laws of diffusion and allows determining hydrogen diffusion coefficients and surface concentrations by measuring the total amount of absorbed hydrogen as a function of the cylinder height. Total hydrogen contents after charging of several cylinders consisting of quenched and tempered steel 42CrMo4 (1.7225) were measured by carrier gas hot extraction and the applicability of the absorption model on the measurement was demonstrated by mathematical fitting. The diffusion coefficient for this material was determined to be $D = 3.8\ 10^{-11}\ m^2/s$ and the hydrogens surface concentration increases with increasing charging time.

Introduction

Hydrogen embrittlement (HE) is a highly discussed topic in science. Failures can cause crucial damage with severe risks for machines and lives. Therefore, lot of analytical and test methods have been developed in recent years to understand the mechanisms of HE and to assess the susceptibility of different metals to HE. Mechanical test methods, e.g. slow strain rate tests (SSRT), step-load tests (SLT) and creep rupture tests (CRT), require a sufficient critical amount of absorbed hydrogen into the material in order to cause the hydrogen induced damage [1–10]. Hence, hydrogen charging is an essential step in the research of HE. Hydrogen charging can be performed from gas or liquid phases [11,12]. It is known that hydrogen absorption and embrittlement are much more pronounced in sour aqueous environments, rather than in the gas phase [11]. In sour aqueous environments, e.g. a pickling solution, discharged atomic hydrogen is provided by the reduction of solvated hydrogen ions according to the Volmer mechanism
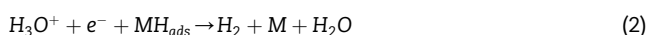
$$H_3O^+ + e^- + M \rightarrow MH_{ads} + H_2O \qquad (1)$$

where MH_{ads} refers to the adsorbed state of the reduced hydrogen at the metallic phase M [13]. The hydrogen discharge process is followed by two reactions, the hydrogen

evolution reaction (h.e.r.) according to the Heyrovsky mechanism

$$H_3O^+ + e^- + MH_{ads} \rightarrow H_2 + M + H_2O \qquad (2)$$

and the hydrogen absorption reaction (h.a.r.)

$$MH_{ads} \rightarrow MH_{abs} \qquad (3)$$

The reduction reaction according to equation (1) is accompanied by the oxidation of the metallic phase

$$M \rightarrow M^+ + e^- \qquad (4)$$

where cations M^+ can pass into solution [11].

Equations (1)—(4) do not show the whole complexity of the hydrogen charging process at all. There are many other processes taking place at the sample's surface and in the bulk influencing the hydrogen charged state of the component, e.g. the formation of a capacitive electrochemical double-layer, diffusion processes and trapping of hydrogen atoms at energetically favourable sites in the bulk [11,14]. These processes determine the degradation of the mechanical performance of the hydrogen charged components and thus influence the results of the mechanical test methods. Therefore, a detailed description of the hydrogen charged state is crucial for the interpretation of mechanical test parameters and the interpretation of HE.

At present, there is no method describing the hydrogen charged state of components in detail. By means of a Devanathan-Stachursky electrochemical cell hydrogen permeation through thin sheets can be measured [15—17]. This allows determining the hydrogen diffusion coefficients and kinetics of hydrogen discharge and entry reactions neglecting the recombination reactions. The method also allows modelling the amount of absorbed hydrogen and its trapping state [18]. However, the limitation of permeation tests to thin membranes and the elaborate preparation of these membranes including coating the anodic side with palladium, make it difficult to apply permeation tests reproducibly and to refer the results to bulk materials [11].

A widely used method to determine the amount of absorbed hydrogen in bulk materials is carrier gas hot extraction (CGHE) [23]. CGHE is a powerful method for measuring even small amounts of hydrogen in metals. It provides hydrogen effusion at various temperatures up to the melting temperature of the metal where the effused hydrogen is quantified by means of a thermal conductivity detector or by a quadrupole mass spectrometer. Thus, the total amount of absorbed hydrogen can be determined in dependency on the activation temperature for desorption [19,20]. However, the hydrogen distribution over the cross section of the component is not necessarily constant, since it depends on diffusion and trapping processes. In order to refer crucial hydrogen concentrations to hydrogen embrittlement it is appropriate to state a concentration distribution over the cross section rather than a total absorbed hydrogen content.

The concentration distribution is a solution of Fick's laws of diffusion [21,22]. For the one-dimensional case of non-steady state diffusion Fick's law can be stated as

$$\frac{dc}{dt} = D \cdot \frac{d^2c}{dx^2} \qquad (5)$$

where x is the spatial coordinate, D the diffusion coefficient, t the charging time and c the concentration [22]. In the case of a plane sheet with thickness h, where the hydrogen concentration in the region $-h/2 < x < h/2$ is initially zero and the surfaces are kept at a constant hydrogen concentration c_i a solution of equation (5) is

$$\frac{c}{c_i} = 1 - \frac{4}{\pi} \cdot \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cdot exp\left(\frac{-D(2n+1)^2\pi^2 t}{h^2}\right) \cdot cos\left(\frac{(2n+1)\pi x}{h}\right)$$

$$(6)$$

note that equation (6) is a converging series and is symmetric about the centre axis of a plane [22]. If H_t is the total amount of absorbed hydrogen at charging time t and H_∞ the corresponding quantity after infinite time, then

$$\frac{H_t}{H_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \cdot exp\left(\frac{-D(2n+1)^2\pi^2 t}{h^2}\right) \qquad (7)$$

Experimentally, the application of equation (7) allows to determine H_∞ and D by varying the charging time t or the thickness h of a plane sheet after hydrogen charging at a time-independent surface concentration c_i and measuring H_t by CGHE [22]. Due to the kinetics of the surface reactions (equations (1)—(4)), c_i is assumed to be time-dependent. Therefore, it is more appropriate to vary the thickness h for several charging times than to vary the charging time for a constant sample thickness. A problem in varying h is that with increasing h the lateral area of the sample increases and contributes strongly to the total absorbed hydrogen amount after immersion into a charging solution. Thus, it is unreasonable to work with a mathematically exact one-dimensional solution of Fick's law, particularly as it is a converging series, which has to be performed for a sufficient number of n to ensure correct values for H_t/H_∞ as shown in equation (7).

The focus of this study is to present a hydrogen absorption model according to Fick's laws which coincides well with the performed CGHE measurements after immersing cylindrical samples of a quenched and tempered steel 42CrMo4 of grade 12.9 into a charging solution of 9 % HCl blended with $3 g/l Na_2S$ as hydrogen absorption promotor. The model is based on an approximate solution of Fick's laws and takes into account the absorption over the base areas as well as over the lateral area of the samples. By applying the hydrogen absorption model onto the measured data points, three parameters can be achieved, which describe the spatial hydrogen distribution after charging, e.g. the hydrogen surface concentration c_i, the diffusion coefficient D and the total amount of absorbed hydrogen per unit of the lateral area H_{A_L}. At present, no work is known describing the hydrogen charged state in detail by applying Fick's laws of diffusion onto the data of CGHE measurments.

Development of the hydrogen absorption model

Conventional CGHE measurement determine the total hydrogen content H (in μg) by melting the specimen. The total hydrogen content H depends on the h.a.r. and on diffusion