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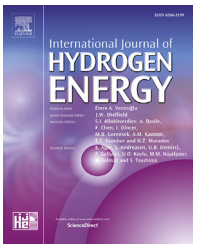

Aggregation of experiments for estimation of hydrogen permeability parameters

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ABSTRACT

The study of the hydrogen permeability of materials employs a variety of methods with their own specific features, advantages and drawbacks. The penetration method allows determining the diffusion coefficient from so-called lag time. The accuracy of the estimation depends on the degree of proximity to the DLR (diffusion limited regime) mode. The method of 'communicating vessels' is more sensitive to surface processes. 'Separate' application of these methods leads to a situation where the materials studied are in fact somewhat different (for example, due to different impacts on the surface), and significant differences in parameter estimates ensue. This paper suggests and implements a cascade experiment technique and the corresponding mathematical toolkit. The informative capacity of experimental studies and the accuracy of the estimation of hydrogen permeability parameters (diffusion, absorption, desorption) are thus enhanced.

Introduction

Studies on the interaction of hydrogen isotopes with structural materials are mainly necessitated by problems in the energy industry, metal protection from hydrogen corrosion and the design of chemical reactors [1–10]. Different alloys, which may be suited for use in gas-separation plants for the membrane technology of high-purity hydrogen production, were investigated by measuring specific hydrogen permeability. For the structural materials one had to estimate the parameters of diffusion and sorption to numerically model the different scenarios and experimental conditions of the material usage (including extreme ones), and identify the limiting factors. Some particular problems of the hydrogen materials science and corresponding mathematical models related to the topic of this study were investigated in Refs. [11–15]. The models of multichannel diffusion and nonlinear thermal diffusion are presented in Refs. [16,17].

Experiments show that the limiting factors are diffusion processes as well as physical and chemical phenomena at the surface [1,2]. The transfer parameters depend on the specifications of the material batch production process. It is therefore unreasonable to target at 'tabular data'. Instead, effective algorithms for processing experimental curves are necessary. In this study, we consider the permeability model taking into

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account the main factors and the self-descriptiveness of the experiment.

The penetration method (where a sufficiently high pressure of hydrogen gas is built up in steps at the inlet side of the test material membrane, and the penetrating flux is determined in the vacuum created at the outlet side) allows determining the diffusion coefficient from so-called lag time. The accuracy of the estimation depends on the degree of proximity to the DLR (diffusion limited regime) mode. The method of 'communicating vessels' (where hydrogen from the input volume seeps through the membrane to the isolated output chamber, and the change of pressures is measured) is more sensitive to surface processes. 'Separate' application of these methods leads to a situation where the materials studied are in fact somewhat different (due to different sample pre-treatment procedures). This fact is one of the reasons for the differences in the estimates of hydrogen permeability parameters.

The main idea of this study is to develop an aggregation procedure for hydrogen permeability experiments precluding depressurization and (or) alteration of the samples of the investigated material. It also implies a corresponding mathematical software for correct processing of the measurements along with appropriate assembly of the experimental unit.

Another important consideration is the uniqueness of the parameter estimates of the investigated model. The results obtained on thin laboratory samples are extrapolated to 'walls' when justifying the choice of, for example, structural materials for the ITER project. Uniqueness allows for a correct recomputation. In the above-mentioned context the aggregation of experiments allows to make the measurements substantially more informative for further estimation of the parameters of bulk and surface processes in their dynamic interplay.

Experiment

Description of the experimental set-up

Fig. 1 represents the flowchart of a high-vacuum unit 'Protium' for studying hydrogen permeability, developed at the Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences in collaboration with the Physical Research Institute of the Saint Petersburg State University. The unit consists of the following modules – a rough pumping system, a finishing pumping system, an inlet system, a control system, a measuring system, and a diffusion cell.

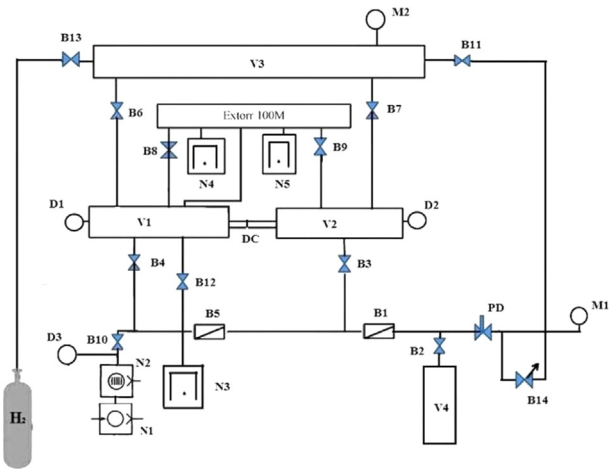

Fig. 1 – 'Protium' unit flowchart.

The rough pumping system includes an oil-free exhaust cart HiCube 80 manufactured by Pfeiffer Vacuum Inc. The exhaust unit incorporates a membrane (N_1) and a turbomolecular (N_2) pumps that create an initial vacuum of up to 10^{-8} Torr, and the butterfly valves B_1, B_5 and B_{10}. The pressure in the system in the mode of sample preparation for the experiments was measured by a magnetron gauge (D_3) WRG-S manufactured by Edwards (from atmospheric pressure down to 10^{-9} Torr).

The system of finishing pumping can build a vacuum of 10^{-9} Torr. This system includes pumps manufactured by the company Varian Vacuum Technologies – VacIon 150 Plus Diode (N_4 and N_5) and a Penning-type pump Diode –0.25–1 (N_3), as well as the UHV valves B_6–B_9 and B_{12}, which connect the pumps to the diffusion cell, an inlet bulb (V_3) and the mass spectrometer Extorr XT100M. The system provides a hydrogen pumping rate of $V_{pump} \approx 80$ l/s. Pressure in the finishing pumping system is measured by a vacuum controller TIC 6 with the gauges D_1 and D_2 provided by the Edwards company.

The inlet system, consisting of bulbs (H_2) with ultrapure hydrogen (99.9999%), a preliminary hydrogen inlet (V_3) and the vacuum valves B_{11}, B_{14}, B_2, permits to supply hydrogen to the volume (V_4) between the butterfly valves B_1 and B_{14}, whereas the pressure is measured by the dial gauge M_1 manufactured by Edwards (the range is 0–760 Torr). The butterfly valves B_1 and B_5 can create a pressure spike on the right or on the left side of the membrane through the UHV valves B_4 or B_3, respectively. Before hydrogen goes to the diffusion cell it can be cleaned from impurities by means of a Pd-Ag-based filter. The calibration bulb (V_4) of known volume (1000 cm^3) is used for measuring the enclosed volumes V_1 and V_2 at the inlet and the outlet sides of the membrane.

The system of controlling and maintaining constant hydrogen pressure in the inlet chamber is based on a VAT manufactured inlet valve and Edwards-manufactured pressure vacuum gauges. Besides, one can install an absolute pressure controller 640 MKS Instruments with a digital power supply R4000B-F in order to maintain pressure in the inlet chamber at no more than 1000 Torr with an error of ±2.2 Torr. The pressure in the inlet and the outlet volumes V_1 and V_2 of the diffusion cell is measured by the vacuum gauges D_1 and D_2 automatically with the help of the TIC PC Monitor software. The range of the measured pressures is 0–1000 Torr, the deviation of the measurements is 0.1 Torr. Hydrogen partial pressures are recorded by the mass-spectrometer Extorr XT100M.

The diffusion cell is assembled of two cylindrical tubes with a membrane in between. The clamping jaws of the tubes have an oval bevel securing vacuum-tight coupling of the tubes via copper gaskets 0.2 mm thick. The two parts of the diffusion cell are bolted together by four screws. At the ends of the diffusion cell stand we installed two flanges that fix the cell to the unit. The outer diameter of the membrane is 15 mm.

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