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Short Communication

The advantage of using in-situ methods for studying hydrogen mass transport: Neutron radiography vs. carrier gas hot extraction

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ABSTRACT

Neutron radiography (NR) is compared with the commonly used carrier gas hot extraction (CGHE) technique. We performed isothermal hydrogen effusion experiments at 623 K to study the mass transport kinetics. The investigated material was technical iron. The quantification of the hydrogen mass flow is done for NR by using concentration standards. The temporal hydrogen concentration evolution in the sample coincides well for both methods, i.e. NR and CGHE, and is in good agreement with literature. The advantages of the NR method are the non-destructive nature of measuring and the in-situ determination of hydrogen concentrations with high spatial and temporal resolution. Remaining hydrogen inside the sample can be identified directly by the NR method.

1. Introduction

Hydrogen can influence significantly the durability of Fe-based alloys by degrading the mechanical properties with subsequent hydrogen-assisted cracking [1]. Hydrogen uptake of the material may occur via the protection gas during arc welding. Thus, having accurate information about the amount of hydrogen and its distribution in the material as well as about the kinetics of hydrogen mass transport is essential for revealing the underlying transport [2] and damage mechanisms [3].

Conventionally, small amounts of hydrogen are measured by carrier gas hot extraction (CGHE) [4] at concentrations in the order of 1 parts per million by weight (wt.ppm). Sample preparation requires cutting small pieces out of the component. Then the sample is annealed isothermally in steps even above melting temperature (melt extraction). Correlating sample temperature at which hydrogen is released to binding energies from literature may allow to backtrack the so-called 'traps' where hydrogen was located, e.g. at grain boundaries or non-metallic inclusions [5].

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Non-destructive radiation techniques have been already used to measure hydrogen in metals. Hanada et al. [6] used, for instance, tritium autoradiography to measure local hydrogen concentration profiles around imperfections in tempered martensitic steel. Although concentrations as small as 0.1 wt.ppm could be detected, the time resolution was in the order of some 10 min. Révay et al. [7] used prompt γ activation analysis to measure hydrogen in catalytic reactors at concentrations in the wt.ppm range but with limited spatial (~0.2 mm) and temporal (~hours) resolution.

Neutron radiography (NR) is a modern non-destructive in-situ imaging method with a wide field of applications in material science, physics, biology, and archaeology [8], which is available worldwide at numerous research institutions. New detector techniques and high flux neutron sources allow with appropriate normalization of the images to measure quantitatively, e.g. fast dynamic processes like hydrogen diffusion in metals [9] or the flow of water or hydrogen in fuels cell membranes [10]. In our particular case we used both the conventional CGHE and this NR imaging technique to measure the effusion behaviour of hydrogen in technical iron. We compare and discuss the results with respect to the advantage of using modern in-situ techniques for studying hydrogen mass transport phenomena.

2. Experimental details

With both methods, i.e. CHGE and NR, isothermal heat treatments of hydrogen-charged samples were performed. A detailed description of the methods can be found in sections 2.2 for CGHE and 2.3 for NR. Fig. 1 shows the measurement principle of both methods.

2.1. Sample preparation

Technical iron (ARMCO™) samples with an average grain size of 80 μm were cut (40 × 5 × 2 mm^3) from a rolled plate with subsequent grinding and polishing of the surface to a final surface roughness of 1 μm. The electrochemical hydrogen charging was carried out in an electrolytic cell with 0.05 M H_2SO_4 as electrolyte and 0.1 M $NaAsO_2$ as inhibitor to prevent recombination of hydrogen at the sample surface. The current density was 100 A/m^2 applied for 48 h to fully saturate the cathodically connected sample. Samples storage was in liquid nitrogen to minimize hydrogen losses before the measurements. The total amount of hydrogen introduced was 30 wt.ppm measured by melt extraction at temperatures up to 1800 K using a LECO TCH 600 with infrared sensor.

2.2. Carrier gas hot extraction

The hydrogenous sample is put in the pre-heated furnace to achieve a fast heating up to 623 K with subsequent isothermal annealing. An inert gas flow carries the released molecular hydrogen from the furnace to a sensor, which measures the heat conductivity of the gas mixture. A commercial CGHE system was used from Juwe™ (model H-MAT 221).

The heat conductivity depends on the hydrogen concentration in the gas. The sensor's signal is normalized with the sample weight giving the hydrogen concentration in wt.ppm. Other sensor types (e.g. mass spectrometer or semiconducting devices) allow measuring hydrogen concentrations below concentrations of 1 wt.ppm. The spatial resolution of CGHE is limited to the sample size (typical initial weight for Fe approx. 30 g).

2.3. Neutron radiography

In first transmission experiments we could show that NR is suitable for measuring the effusion of hydrogen if a reference and standards are used [9]. The measurement set-up is described in detail in [11].

In general, the attenuation behaviour of matter is described by the Lambert–Beer Law, $I = I_o \exp(-\mu d)$, with I, the transmitted intensity, I_0 the initial intensity, μ the neutron attenuation coefficient and d the total thickness of the sample in flight direction of the neutrons.

The acquisition of transmission images was performed at ANTARES, the neutron imaging facility of the research centre Heinz Maier-Leibnitz (FRM II). The detection system consists of a neutron-sensitive scintillation screen with Cu and Ag doped ^{6}LiFZnS filmed by a Peltier-cooled 2048 × 2048 $pixel^2$ CCD camera (Andor DW436N-BV) with 16-bit signal resolution yielding a final effective pixel size of 70 μm. The neutron flux

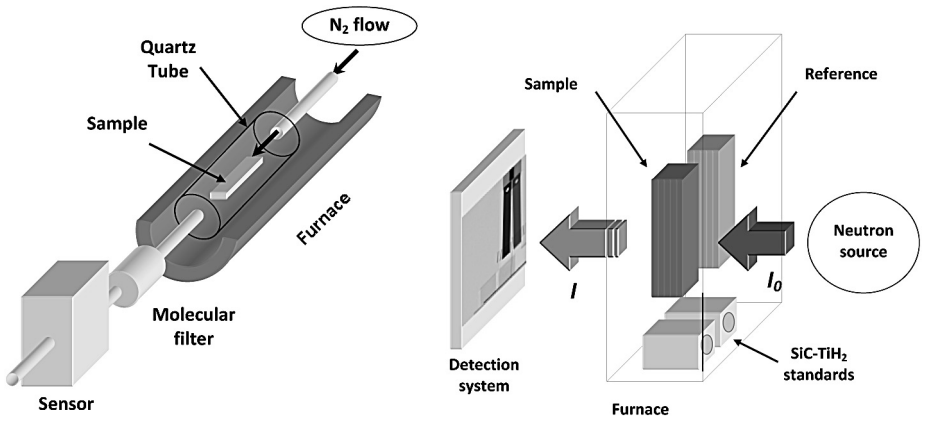

Fig. 1 – Measurement principles of carrier gas hot extraction (left) and neutron radiography (right).