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Neutron transmission measurements on hydrogen filled microspheres

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ABSTRACT

Hollow microspheres are promising candidates for future hydrogen storage technologies. Although the physical process for hydrogen diffusion through glass is well understood, measurements of static quantities (e.q. hydrogen pressure inside the spheres) as well as dynamic properties (e.g. diffusion rate of hydrogen through glass) are still difficult to handle due to the small size of the spheres ($d \approx 15$ µm). For diffusion rate measurements, the long-term stability of the experiment is also mandatory due to the relatively slow diffusion rate. In this work, we present an accurate and long-term stable measurement technique for static and dynamic properties, using neutron radiography. Furthermore, possible applications for hydrogen filled microspheres within the scope of radiation issues are discussed.

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1. Introduction

Hydrogen is by far the most promising energy carrier of the future. Due to its usage in fuel cells, where the efficiency is very high and still increasing, and its practically limitless availability on earth, hydrogen might be the most important energy carrier for alternative, renewable energy sources. The FOTEC Company is concentrating on different hydrogen storage technologies, especially on complex metal hydrides and the above mentioned hollow glass microspheres. While for metal hydrides, storing of hydrogen is achieved by chemical bonding to the hydride ($NaAlH_4$, $LiBH_4$, etc.), hollow microspheres allow for gaseous storage of hydrogen (along with some other light elements). This is achieved by heating up the spheres within a hydrogen atmosphere at a constant pressure. Hydrogen diffuses through the glass wall and after reaching the desired pressure, the spheres are cooled down and diffusion stops (or is drastically reduced) [1]. Although the diffusion process through glass is well understood, measurements of diffusion rates are still difficult to handle. This is mainly due to the small size of the spheres and the required long-term stability of the measurement. In cooperation with the Atomic Institute in Vienna, we present a method for pressure and diffusion rate measurements at high accuracy and the potential for spatial resolution of diffusion pro-

cesses for hydrogen filled microspheres. The method is based on neutron radiography (NR) as described below.

2. Hydrogen filling of microspheres

For this experiment we used S38HS microspheres from company 3M™ with an average diameter of approx. 15µm (Fig. 1). Within a closed steel cylinder, constant hydrogen pressures (20, 25, 40 bar) were applied at a temperature of 190 °C. The final pressure was measured using thermo gravimetric analysis (TGA). In order to achieve a high throughput of samples, we fixed the filling time to a maximum of 3 days. After that, the microspheres were cooled down to room temperature and brought to the reactor. Special aluminium sample holders were used in order to reduce scattering of neutrons within the sample holder. Transmission of neutrons through the sample was measured over several days for different initial pressures at room temperature. Since S38HS microspheres show a non-negligible diffusion rate at room temperature for a reasonable time interval (several days), we were able to follow the exponential decrease of the neutron attenuation, which actually proves the feasibility of the NR method.

3. The neutron radiography method

The application of neutron radiography for hydrogen studies has a long tradition at the Atomic Institute operating a 250 kW TRIGA MARK II reactor [2,3] (Fig. 2). Digitized neutron imaging can be offered with different spatial resolutions [4,5]. The transmission experiments were performed using a 100 µm thick ^6LiF

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E-mail addresses: dyrnjaja@ati.ac.at (E. Dyrnjaja), hummel@fotec.at (S. Hummel), keding@fotec.at (M. Keding), marie-theres.smolle@tuwien.ac.at (M.-T. Smolle), gerger@fotec.at (J. Gerger), zawisky@ati.ac.at (M. Zawisky).

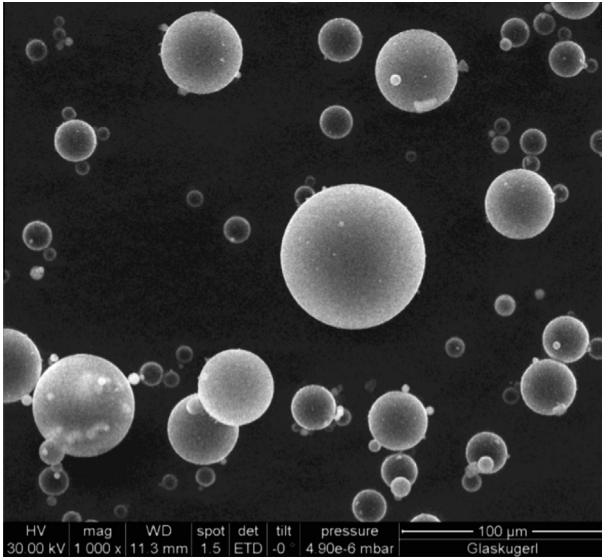**Fig. 1.** SEM image of S38HS Hydrogen filled microspheres.

scintillator layer with 150 μm spatial resolution. The detection process including a Maxwellian energy distribution of the thermal neutrons has been implemented in our MCNPX simulation program [4].

The hollow microspheres were filled with hydrogen gas at FO-TEC Lab under different pressures (20, 25 and 40 bar). The high scattering cross-section of hydrogen yields a high detection sensitivity by neutron radiography (Fig. 2 right) [6–9], hence the neutron attenuation is dominated by the hydrogen content in the sample while neutron absorption in glass is negligible. The neutron attenuation is characterized by the sample thickness d and the total macroscopic cross section Σ and can be approximated by an exponential law (T = transmission probability):

$$1 - T \cong 1 - e^{-\Sigma_{total}d} \qquad (1)$$

It is convenient to use the total macroscopic cross section $\Sigma_{total} = N\sigma = \Sigma_s + \Sigma_a$ (scattering + absorption), where N represents the number of nuclei per volume and d being the sample thickness; the scattering behavior of hydrogen as "free-gas" can be described by a simplified "pinball" model. The cross sections of hydrogen for thermal and cold neutrons are especially high in the low neutron energy range. For hydrogen as a free gas, the cross section for the relevant energy range is taken from evaluated nuclear data file ENDF-VI extracted from MCNPX data libraries [10]. In case of hollow microspheres, the cross section is dominated by single and

multiple scattering [11]. Multiple scattering occurs if the sample thickness d approaches the neutron's mean free path length $L = 1/\Sigma_{total}$; $\Sigma_{total} = \Sigma_H + \Sigma_{Glass}$ [8,11–14]. From the measured Σ one derives a typical mean path length of L = 18 cm and $d/L = 0.05$ in the sample which indicates that multiple scattering is negligible. In a 10 cm sample-to-detector distance no scattering artefacts are detected, only a slight transmission enhancement of 0.1% at 1 cm sample distance.

4. Theoretical considerations

The experimental transmission probability of neutrons is given by:

$$T_{exp} = \frac{I_s - I_b}{I_o - I_b} = e^{-\Sigma_{total}d} \qquad (2)$$

I_s is intensity behind the sample, I_b the background intensity and I_o is the open beam intensity, all averaged in a selected area of interest (AOI). To quantify the hydrogen content inside the microspheres one has to measure the hydrogen loaded and the empty sample. The density ρ_H can then be derived from:

$$T_{Hydrogen} = \frac{I_{filled}}{I_{empty}} = e^{-\Sigma_H d} = e^{-\left(\frac{\rho_H \sigma_H}{N_A d}M_H\right)} \qquad (3)$$

where N_A is Avogadro number, σ_H is the neutron cross section of H as free gas (data retaken from ENDF-VI) [8]; M_H is the atomic weight of H. The density is directly coupled to the pressure inside the spheres

$$P = \frac{\rho_H}{M_H}k_bT. \qquad (4)$$

By using a reference density ρ_{ref} for hydrogen gas at 1 bar and 300 K, Eq. 4 can be written as

$$\frac{P}{P_{ref}} = \frac{\rho}{\rho_{ref}} \qquad (5)$$

where P is the pressure inside the spheres and $P_{ref} = 1$ bar. Using Eq. 5, one directly derives the pressure by inserting the hydrogen density shown in (Fig. 4) (right). This yields a starting pressure on day 1 of approx. 24 bar for the red curve in (Fig. 3) which is in good agreement with the applied pressure during the filling of the hydrogen (25 bar). According to Eq. 5 and (Fig. 4) we derive an exponential decrease of the pressure:

$$P(t) = P_0 - \Delta P\left(1 - e^{-\frac{t}{\tau}}\right) \qquad (6)$$

with $P_0, P(t)$ being the initial and actual pressure of the filled microspheres respectively, P_{ref} is the surrounding pressure (1 bar), ΔP is the pressure difference of P (t) and P_{ref} and
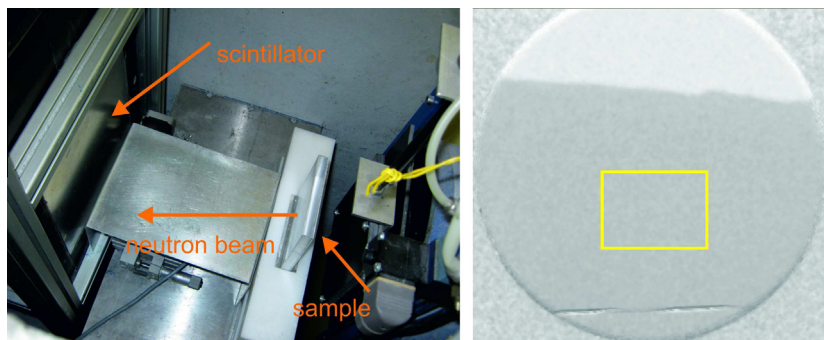

Fig. 2. Left: Setup of the neutron transmission experiment. The distance between sample and detector is 10 cm, in order to avoid scattering artefacts. Right: Neutron radiography image of hydrogen at 20 bar and room temperature, according to Eq. 3. The rectangular area shows an area of interest (AOI).