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Investigations of the structural stability of metal hydride composites by in-situ neutron imaging

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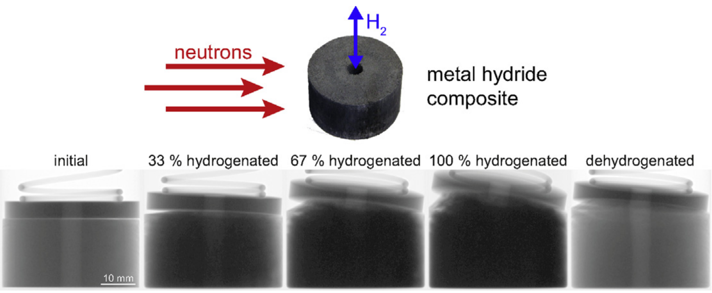
HIGHLIGHTS

- In-situ imaging of metal hydride composites (MHC) with cold neutrons was performed.
- A swelling of 20–33 vol.-% of MHC upon hydrogenation was measured.
- MHC remain mechanically intact even if axial expansion is allowed.
- The heat transfer was improved by closing the gap between MHC and the container.
- Hydrogenation reaction fronts were directly observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal hydride composites (MHC) with expanded natural graphite (ENG) exhibiting enhanced thermal conductivity and reduced porosity compared to metal hydride powders can enable a reversible, compact and safe way for hydrogen storage.

In this study, neutron imaging during cyclic hydrogenation was utilized to investigate the structural stability and the spatial-temporal hydrogen concentration of application-oriented MHC with 40 mm in diameter compared to a loose metal hydride powder. In particular, swelling and shrinking effects of a radially confined MHC which could freely expand upwards were studied. It was found that the loose powder bed was easily torn apart during dehydrogenation, which leads to increased thermal resistance within the hydride bed. In contrast, the thermal resistance between MHC and container wall was minimized since the initial gap closes during initial hydrogenation and does not reopen thereafter. Further cyclic hydrogenation caused MHC volume changes, i.e. an almost reversible swelling/shrinking (so-called “MHC breathing”). Moreover, neutron imaging allowed for the observation of reaction fronts within the MHC and the powder bed that are governed by the heat transfer.

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1. Introduction

Hydrogen offers a much higher heating value per mass[1] than conventional fuels. Therefore, hydrogen technologies might replace carbon-based fuel technologies in the future [1,2]. A hydrogen-based energy cycle could start with the production of hydrogen using a renewable energy source and end with its consumption at a later time at a different location, which is why hydrogen storage is important. Hydrogen gas at standard conditions has a very low mass density of about 89 mg/l. In order to reach useful volumetric capacities, different hydrogen storage technologies have been developed that rely on pressurization (up to 700 bar), on liquefaction at cryogenic temperatures (20 K), on adsorption in porous materials such as metal-organic frameworks (MOFs) or on chemical absorption, for example in hydrides [3]. Metal hydrides (MH) offer very high theoretical volumetric hydrogen storage densities[2] in the range of 100 g-H_2/l. MH are formed at low hydrogen gas pressures (several bars to a few tens of bars) and, for many transition metal (TM) alloys, MH are formed close to ‘room temperature’ (e.g. Fe–Ti-, Ti–Mn-, La–Ni-based hydrogen absorbing alloys) [4,6]. TM-based hydrogen absorbing alloys are advantageous whenever highest volumetric storage capacities are needed but low weight is not mandatory. Therefore, applications in the fields of backup power, materials handling (forklifts), marine or submarine are promising [7]. In this work, a commercially available AB_2-type Ti–Mn-based hydrogen-absorbing alloy called Hydralloy $C5_2$ was used, which absorbs hydrogen up to about 1.8 mass-% [8].

MH are often granules or powder. Because of the large volume content of porosity in powder beds (up to 70 vol.-%), the high volumetric storage capacity of MH vanishes. Moreover, the reduced thermal conductivity of MH powder beds lower the loading and unloading dynamics of respective storage tanks, despite the often extremely fast intrinsic reaction kinetics of TM-based hydrogen absorbing alloys [9,10]. In order to improve the heat transfer and maintain high volumetric storage capacities graphite-containing metal hydride composites (MHC) are considered promising materials for solid-state hydrogen storage [11–15].

In this work, MHC based on Hydralloy $C5_2$ and expanded natural graphite (ENG) are investigated. During cyclic hydrogenation MHC are strongly influenced by crystal lattice expansion and contraction during hydrogenation and dehydrogenation, respectively [16]. In our previous work, we observed a high geometrical stability of MHC in combination with sufficient thermal conductivity and gas permeability throughout cyclic hydrogenation [15]. However, the MHC were cycled while being spatially confined by a strong metallic clamp that resisted the forces generated during hydrogenation and prevented macroscopic swelling of the MHC. This paper addresses swelling and shrinkage of MHC inside a cylindrical tank during cyclic hydrogenation and their non-destructive examination by in-situ by neutron imaging. In contrast to X-rays, hydrogen shows one of the highest attenuation coefficients for neutron radiation [17,18]. Hence, neutron imaging is very sensitive to the detection of hydrogen in materials [19–26]. Previously, we investigated a powdered $LaNi_5$-based hydride and the activation behavior of such MHC by high-resolution neutron imaging using small samples of 12 mm diameter [19,27]. In this work, the investigations focus on application-oriented MHC of 40 mm diameter in comparison to loose hydride powder beds. Both volume changes of the MHC and the spatial-temporal hydrogen concentration profile during cyclic hydrogenation are studied.

2. Experimental

2.1. Sample preparation

The AB_2-type hydrogen absorbing alloy Hydralloy $C5_2$ (51 mass-% Mn, 28 mass-% Ti, 14 mass-% V, 3 mass-% Fe, 3 mass-% Zr) purchased in form of granules from *GfE Metalle und Materialien GmbH* was milled for 5 min under argon using a rotation disk mill. Thereafter, MHC were fabricated as described in our previous work [15] by blending the Hydralloy powder with 5 mass-% ENG. The mixture was then uniaxially compacted into cylindrical solid bodies (pellets) using a die of 39 mm diameter (cf. Fig. 1a). After applying a compaction pressure of 75 MPa a residual porosity of 32 vol.-% remained within the consolidated MHC (88 g total mass). For an equal axial hydrogen distribution, a central hole of 6 mm diameter was manufactured already during compaction by applying a core rod. One of the MHC samples was cut into halves vertically (cf. Fig. 1a). Moreover, a powdered sample was prepared by blending Hydralloy powder with alumina powder (Alcoa, 0.2–0.6 mm) in equal volume fractions (50:50 vol.-%). Alumina has a low attenuation coefficient for neutrons and does not react with hydrogen under the experimental conditions applied. Therefore, it is a suitable filler material to reduce the effective hydrogen concentration in the powdered sample for an improved imaging quality. All processing steps were performed in an inert atmosphere to avoid any surface passivation of the materials involved. The three different types of samples will be referred to as ‘MHC’, ‘half-MHC’ or ‘hydride-alumina powder (HAP)’ samples.

The samples were placed into aluminum alloy (AlMg3) containers (cf. Fig. 1a), which are almost “transparent” for neutrons. The temperature of the container wall was monitored by a thermocouple close to the sample. A moveable 5 mm or 10 mm thick steel plate was placed on top of the MHC samples. The position of the midpoint of the bottom side of the moveable steel plate was used to calculate the volume change of the MHC. For MHC samples, a spring with a modulus of 12 N/cm was integrated into the sample container. This caused a mechanical pressure of at the most 0.03 MPa onto the MHC sample, which is negligibly small compared to the compaction pressure of 75 MPa and, thus, no further densification of the MHC is expected. Both the spring and the steel plate were added to keep the MHC at the bottom of the container during transportation and throughout all experiments (especially during rapid pressure releases) and to keep the MHC in shape in case loose parts or MHC fragments during cyclic hydrogenation occurred (cf. our previous work [27]). For the powdered sample, no spring was used. Instead, since loose powder is much more volatile than a compacted sample, the free volume above the powder was filled with glass fiber wool. This prevents powder material removal from the container to prefilter the gas during H_2 pressure release. In order to allow for a comparison between the results of the powder sample with the MHC no spring was integrated into the container when holding the half-MHC. To stabilize the half-MHC a thin aluminum plate was placed vertically in the middle of the container serving as a constraint of pellet expansion into the empty half. The samples within the containers were subjected to an activation procedure involving exposition to elevated temperatures (~125 °C) for at least 6 h under hydrogen (99.9999% purity) with varying pressures up to 8 bar. After activation, the MHC samples readily absorb hydrogen. The HAP sample was additionally hydrogenated and dehydrogenated 5 times at room temperature, a state called ‘as-cycled’ in the following.

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[1] Lower heating value of hydrogen: 33.3 kWh/kg; methane: 13.9 kWh/kg; gasoline: 12.4 kWh/kg [1].

[2] Metal hydrides ($Ti_{1.2}Mn_{1.8}H_{3.1}$): 100 g-H_2/l; liquid H_2 (20 K, 1 bar): 71 g-H_2/l; H_2 at 700 bar, 300 K: 39 g-H_2/l [4,5].