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In operando visualization of hydride-graphite composites during cyclic hydrogenation by high-resolution neutron imaging

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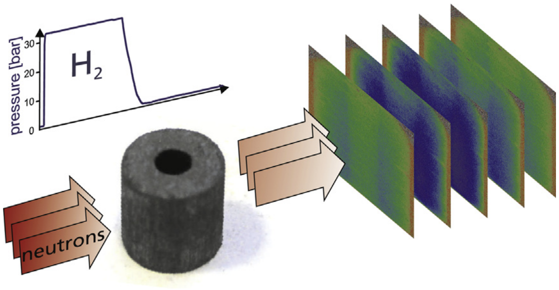
HIGHLIGHTS

- Hydrogenation of hydride-graphite composites (HGC) is visualized *in operando* by neutron imaging.
- Unexpected activation of HGCs through formation of active regions is examined.
- Reaction fronts inside HGCs are visualized for the first time.
- Fast loading and unloading of HGC with hydrogen is realized (<1 min).

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrogen solid-state storage in metal hydrides has attracted remarkable attention within the past decades due to their high volumetric storage densities at low operating pressures. In particular, recently emerged hydride-graphite composites (HGC) can enable a safe, reliable and very compact hydrogen storage solution for various applications. In this regard, only little is known about the activation behavior of such HGC, their cycle stability and degradation effects. Because of the high sensitivity to hydrogen, neutron imaging offers a distinctive approach to examine *in operando* reaction fronts, swelling effects and microstructural changes of hydrogen absorbing materials with high spatial and temporal resolution. In this contribution, a comprehensive analysis of various phenomena during activation and cycling of HGC based on a Ti–Mn hydrogen absorbing alloy and expanded natural graphite is reported for the first time. A neutron radiography and tomography set-up with a spatial resolution down to 7 μm was utilized allowing highest detection precision. During initial hydrogenation, regions with enhanced reactivity are observed which contradicts a theoretically expected homogeneous reactivity inside the HGC. These active regions grow with the number of hydrogenation-dehydrogenation cycles until the whole HGC volume uniformly participates in the hydrogen sorption reaction. With regard to long-term hydrogenation-dehydrogenation cycling, inhomogeneous swelling effects were observed from which essential conclusions for technical HGC-based tank systems can be derived.

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1. Introduction

Renewable energy sources are gaining importance, which is why the development of environmentally friendly energy storage and energy distribution technologies is essential [1–3]. In this respect, hydrogen is a clean, safe and carbon-free energy carrier for portable, mobile as well as stationary applications [4–9]. A hydrogen-based energy cycle demands for efficient, compact and safe storage solutions [10]. Due to high hydrogen storage capacities and moderate operating pressures, metal hydrides have increasingly attracted attention within recent years [11–14].

Although a large number of hydride-forming metallic alloys is known [15,16], only a few are in commercial use, for example La–Ni, Ti–Mn and some Mg alloys [17–19]. In this contribution, an AB_2-type Ti–Mn alloy (also called Hydralloy® $C5_2$) was used which is already in commercial application, for example, for maritime fuel cell applications [18]. Hydralloy® $C5_2$ has a gravimetric hydrogen storage capacity of about 1.8 wt.%-H_2 [20] at room temperature combined with a high volumetric hydrogen storage capacity up to 100 g-H_2 l^{-1} [21]. Hydralloy® $C5_2$ can be classified as room-temperature hydrogen storage material because it can be hydrogenated from −20 °C to +60 °C at moderate hydrogen pressures. Moreover, it exhibits very fast intrinsic sorption kinetics [22,23]. Thus, Hydralloy® $C5_2$ is also suitable for thermochemical applications such as non-mechanical hydrogen compressors or actuators where fast system dynamics are needed [24,25]. A further promising application is the thermochemical storage of industrial heat where a Hydralloy®-based solid-bed reactor can be coupled to a high-temperature hydride reactor (e.g. based on MgH_2) to store the hydrogen generated during heat excess times and to release it on demand to rehydrogenate the high-temperature hydride [26,27].

Besides the intrinsic hydrogen sorption kinetics of the storage material, the loading and unloading dynamics of hydride-based storage tanks are further influenced by the heat and gas transport properties of the hydride bed. From the viewpoint of realistic hydride tank systems, the transfer of the reaction heat through the hydride bed is usually the rate-determining step, because loose powder beds are known for inferior heat transfer properties, which is a serious drawback for numerous applications [28,29]. In order to overcome this limitation hydride-graphite composites (HGC) were developed recently. These composite materials exhibit an increased effective thermal conductivity and higher mechanical stability, which, thereby, facilitate handling during fabrication and a markedly improve (un-)loading dynamics of the storage tank. According to the literature, two major routes can provide enhanced heat conduction in a hydride bed. One approach is to embed the hydrogen absorbing alloy in auxiliary metal structures of high thermal conductivity, for example nickel or aluminum fins or open-cellular foams [30–32]. The second approach focuses on composites of hydrogen absorbing alloys and graphite [33–38]. Following this path, the thermal conductivity can be tailored very accurately. In addition, anisotropic heat conduction and strongly increased volumetric storage capacities compared to those of loose powders can be realized using uniaxial compaction techniques. In our previous works [36,37,39,40] we demonstrated that compacted composites of MgH_2, $NaAlH_4$, $LiNH_2$ and Hydralloy® with graphite have superior effective thermal conductivities in the radial direction, which is beneficial when using a cylindrical geometry of the storage compartment. Moreover, the residual porosity of such HGC can be adjusted to meet the requirements of the storage container concerning gas permeability, mechanical stability and geometrical integrity during cycling.

With regard to Hydralloy®-based HGC [40], it was found that during the first hydrogenation-dehydrogenation cycles the hydrogen sorption kinetics as well as the hydrogen storage capacity improve continuously. Furthermore, a change of physical properties such as gas permeability and thermal conductivity with the number of hydrogenation-dehydrogenation cycles was observed. Up to now, it is not clear what causes this behavior and how it affects the long-term performance of the HGC. Since Hydralloy® dehydrogenates at room temperature and atmospheric pressure it is not possible to investigate the properties of HGC in their hydrogenated state outside a reactor. Thus, an *in operando* method of visualization of HGC during cyclic hydrogenation accompanied by a mapping of the hydrogen element distribution inside the HGC can contribute to a better understanding of the hydrogenation behavior of HGC. In turn, such results would allow to draw conclusions on materials production and HGC-based storage tank design.

In this contribution, the behavior of HGC based on Hydralloy® and expanded natural graphite (ENG) concerning their initial hydrogenation cycles in combination with an activation procedure is discussed. In this regard, neutron imaging (radiography and tomography) was used to examine HGC during hydrogenation and dehydrogenation. In contrast to X-rays, neutrons are suitable to investigate processes inside hydrogen absorbing materials [41]. In principle, the attenuation of the neutron beam passing through an object is described by the Lambert-Beer law:

$$I = I_0 e^{-\sum d} \tag{1}$$

where I_0 is an incident beam intensity, Σ is the linear attenuation coefficient and d is the thickness of the irradiated sample. Σ depends on the corresponding scattering and absorption cross-sections and on the density of the scattering centers. For neutrons, Σ is not related to the atomic number of the element in a simple and monotonic way as for X-rays, but depends on the internal structure of the nucleus of the atom under study. Hydrogen nuclei exhibit one of the largest cross-sections among the elements. This provides excellent contrast between hydrogen and common metals such as Al, Ni, Cu etc. For this reason, containers made of aluminum are almost “transparent” for a neutron beam (even for a wall thickness exceeding 10 mm). In addition, Hydralloy® (Ti–Zr–Mn–V–Fe alloy) and graphite are quite transparent to the neutron beam as well.

In our previous work [42] it was reported that hydrogenation of a loose metal hydride powder bed can be examined utilizing

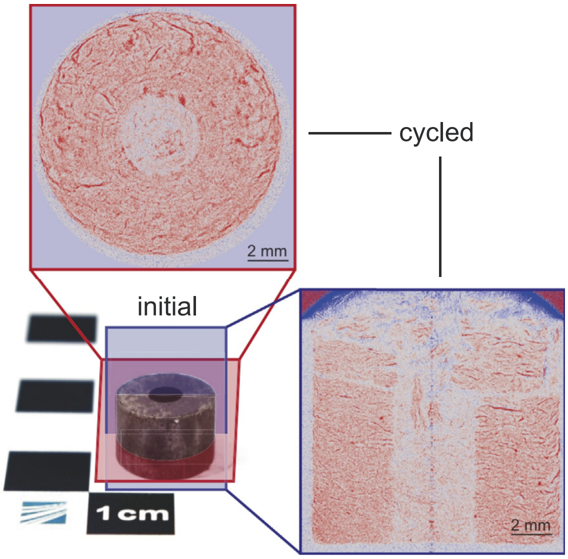

Fig. 1. Hydralloy®-based hydride-graphite composite (HGC) containing 5 wt.% expanded natural graphite compacted at 75 MPa. The horizontal and vertical slices were obtained by neutron tomography of the HGC after 35 (de-)hydrogenation cycles.

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