Mechanical stresses originating from metal hydride composites during cyclic hydrogenation

Felix Heubner [a], Carsten Pohlmann [b], Sebastian Mauermann [b], Bernd Kieback [a,b], Lars Röntzsch [b,*]

[a] Institute for Materials Science, Technische Universität Dresden, Helmholtzstraße 7, 01069 Dresden, Germany
[b] Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Branch Lab Dresden, Winterbergstraße 28, 01277 Dresden, Germany

ABSTRACT

Metal hydride composites (MHC), which consist of a primary hydrogen absorbing phase and secondary phases such as graphite, offer very high volumetric storage densities and operation dynamics compared to widely used metal hydride powder beds.

Here, we report on the stress evolution of confined MHC during hydrogen ab- and desorption which is due to the lattice expansion of the hydrogen absorbing phase during hydrogen uptake. The stress development during hydrogenation was recorded *in situ* using a specially designed measuring cell. Influences of gas pressure, temperature and MHC geometry on the stress evolution were considered. In this regard, so-called *pressure-stress-isotherms* are proposed for the first time in thermomechanical analogy to pressure-composition-isotherms.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Metal hydride technology offers certain advantages over compressed or liquid hydrogen storage solutions [1–4]. It is mandatory to realize safe, efficient and sustainable hydrogen storage systems through technological advancements [5–9]. In general, the risk potential of pressure vessels is derived from the type of fluid stored, its internal volume and the applied pressure. In this context, the comparably low H$_2$ pressures needed for the operation of and the reduced free gas volume inside metal hydride tanks results in a low risk potential [10–12].

The international standard DIN ISO 16111 represents guidelines for the design and construction of metal hydride tanks [13]. Among other features, the volume expansion of the hydrogen absorbing alloy during hydrogen uptake has to be considered. It can be compensated by increased wall thicknesses of the vessel and/or additional expansion space inside the vessel. In this regard, it is recommended to use strain gauges to permit the safe operation of metal hydride tanks. Furthermore, in order to ensure a high safety level of optimum metal hydride storage solutions, it would be desirable to direct the volume expansion of the hydrogen absorbing material during hydrogenation in a controlled manner.

The exothermal absorption of hydrogen in a metal results in a significant expansion of the crystal lattice which originates from interactions between the hydrogen atoms, which are typically located on interstitial lattice sites, and the metal atoms [14]. In the so-called alpha-phase, hydrogen occupies

only a minor fraction of interstitial lattice sites (lattice gas). If the hydrogen concentration in the metal increases, the crystal lattice expands which can be characterised by in-situ X-ray diffraction. For example, Nakamura et al. [15] reported an lattice expansion during the hydrogenation of as-activated $LaNi_{4.8}Fe_{0.2}$ of up to 21 vol.%. It is widely accepted that the lattice expansion causes local stresses inside the bulk of the host metal, which typically causes decrepitation of the bulk resulting in the formation of fine powders [16–18]. With an increasing number of hydrogenation cycles, the metal powder particles may become finer and finer due to repeated decrepitation, which in turn causes an unconfined powder bed to expand. Due to mechanical interlocking between powder particles and potential displacements of powder particles, the overall powder bed expansion is usually larger than the volume expansion of the metal lattice itself. According to literature reports, it is possible to examine the expansion behavior of metal hydride powder beds by determining the deformation of thin-walled storage vessels of cylindrical geometry. Using partially filled pressure vessels with applied strain gauges on different locations, the swelling of the metal powder bed during hydrogenation can be determined quantitatively [19–24]. The deformation of such metallic pressure vessels illustrates impressively the strong forces emerging from the volume expansion of hydrogen absorbing alloys [22]. Other reports describe that it is possible to determine the volume expansion of a metal hydride powder bed using LVDT (linear variable differential transformer) sensors, which measure the dislocation of a punch on the top of the powder bed inside a hydride storage vessel [25,26]. The volume expansion of a cylindrical vessel, filled with metal hydride composites (MHC) based on MgH_2, was measured recently using a dilatometer on the outer surface of the vessel [27]. The examined radial dilatation indicates a significant reduction of the radial stresses on the cylinder wall with increasing graphite content.

In most metal hydride tank systems, free space inside the pressure vessel is reserved, so that the macroscopic volume expansion of the hydrogen absorbing powder bed or of an MHC is fully or partly possible [28]. However, this free volume, which in some cases occupies up to 70% of the volume available inside the vessel, reduces the volumetric hydrogen storage capacity of the metal hydride tank drastically. In order to deduce design criteria for hydride storage vessels with highest hydrogen storage capacities, all influences of the hydrogen absorbing material and the hydrogenation conditions have to be identified. Furthermore, the generation of stresses in the wall of the pressure vessel have to be understood and thoroughly characterized. In this regard, it is of utmost importance to measure the forces generated by the expansion of the absorbing alloy during hydrogenation inside a metal hydride tank without any deformation of the wall of the tank in a direct approach.

In our previous work, the hydride forming alloy Hydralloy® $C5_2$ (AB_2-type Ti–Mn alloy with a maximum volumetric storage capacity of 80 g-H_2 per liter) and Hydralloy®-based MHC, which consist of a primary Hydralloy® phase and a secondary phase such as graphite, were studied thoroughly in view of sample preparation, heat and gas transport characteristics and hydrogenation behavior [11]. In particular, for MHC it is known that heat and mass transfer characteristics crucially depend on the residual porosity inside the MHC as well as the volume content of graphite as secondary phase [29–32]. These two influencing parameters will therefore potentially play a major role for the stress generation originating from MHC during hydrogenation, the in-situ characterization of which is the subject of this paper.

Experimental

Hydralloy® $C5_2$ (51 wt.-% Mn, 28 wt.-% Ti, 14 wt.-% V, 3 wt.-% Fe, 3 wt.-% Zr), a commercially available hydrogen absorbing alloy, was purchased from *GfE Metalle und Materialien GmbH*. The delivered granules (2–10 mm in diameter) were milled, blended with 2.5–12.5 wt.-% expanded natural graphite (ENG, delivered by *SGL Carbon SE*) and compacted using a uniaxial press with compaction loads of 75–300 MPa. In the as-compacted state, the MHC consists of a primary Hydralloy® phase, a secondary ENG phase and residual porosity. Two different sizes of cylindrical MHC bodies (pellets) with 14 mm and 39 mm in diameter of various heights were produced. The whole procedure was performed under inert atmosphere to prevent any surface contamination. The materials processing chain is described in more detail in our previous works [11,12].

In case of the 14 mm MHC pellets, cyclic hydrogenation characteristics were monitored using a thermogravimetric device (magnetic suspension balance by *Rubotherm GmbH*) under gaseous hydrogen atmosphere (99.9999% purity; delivered by *Linde AG*). Before each hydrogenation experiment, a cyclic thermal treatment (100 °C; 5/1.5 bar H_2; 4/1 h; 2-times) was carried out to activate the hydrogen absorbing alloy. The 39 mm MHC pellets were hydrogenated in a special test tank described in detail elsewhere [33]. In order to provide a sufficient hydrogen flow rate into the 39 mm MHC pellet via a hydrogen artery (sintered metal filter), the MHC pellets featured a cylindrical hole (6 mm) in the centre. In this setup the hydrogen mass flow, temperature in the 39 mm MHC pellet and gas pressure were controlled. Due to the high mass of the 39 mm MHC pellet and, thus, to ensure a rapid activation, the activation procedure described above was slightly modified (150 °C, 5/1.5 bar H_2, 15/5 min; 10 times). In the next step, both MHC pellet types were hydrogenated at various temperatures (35 °C–65 °C) and H_2 gas pressures (1.5 bar–50 bar). In addition to the limited expansion space in radial direction given by the confining tank wall, a metallic clamp was used to restrict the axial expansion of the MHC pellets during hydrogenation.

Two different force-measuring techniques were integrated into the hydrogenation reactors. Stress-sensible foils (purchased from *Tiedemann & Betz GmbH & Co. KG*), which were placed between the MHC pellets and the clamp, allowed to measure the maximum stresses in radial and axial direction. Different stress-sensible foils were used in ranges from 0.05 MPa to 300 MPa [34]. After the cyclic load with mechanical stress originating from the hydrogenation-induced MHC volume expansion, it was possible to evaluate the stresses that acted on the foils by the intensity of their red coloration. Thus, it was only possible to evaluate the highest occurred mechanical stresses during the whole procedure. The quantitative coloration analysis was executed with Matlab®. The