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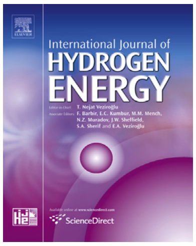

# Long-term cycle stability of metal hydride-graphite composites

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## ABSTRACT

Recently, metal hydride composites (MHC) have been proposed which consist of a hydride forming metal alloy and a highly heat conduction secondary phase such as expanded natural graphite (ENG) in order to improve the thermal conductivity of metal hydride powder beds. However, only little data is available in the literature on the effects of extensive cycling on technically relevant properties of MHC.

In this paper, hydrogenation characteristics, thermal conductivity and geometrical stability of Hydralloy® C5-based MHC were thoroughly investigated over 1000 cycles. The obtained results suggest that the MHC under study did not significantly alter their hydrogen uptake characteristics throughout cycling, despite the fact that their thermal conductivity decreased during the first 250 cycles but remained constant thereafter. Although the cylindrical MHC maintained their geometrical stability, radial cracks were detected after cycling. Based on these results, MHC are suitable for high-dynamic applications such as hydrogen storage or thermochemical devices.

## Introduction

One of the challenges of renewable energy sources is their volatility. Therefore, energy storage technologies are essential in order to meet the actual energy demand. Surplus electricity, for example, can be stored in form of hydrogen following the electrochemical splitting of water. Hydrogen is a versatile secondary energy carrier that can be used in fuel cells, chemical synthesis or combustion when needed. Metal hydrides are a promising option to store hydrogen at high volumetric density, moderate temperatures and low pressures [1–4].

A specific example where metal hydrides can be used for energy storage refers to domestic applications. Here, hydrogen produced by electrolysis using photovoltaic surplus energy can be stored in a metal hydride. At a later stage, hydrogen is released from the metal hydride storage to feed

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*Abbreviations:* MHC, metal hydride composite; ENG, expanded natural graphite.

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**Nomenclature**

| | |
|---|---|
| Δp | differential pressure |
| T | temperature |
| x | hydrogen uptake |

fuel cells to ensure uninterrupted energy supply [5]. Moreover, the heat of the corresponding exothermal hydride formation (absorption) can be used for thermal applications, for example, heating of domestic water (See more in Refs. [6–8]).

For such applications, in addition to a high hydrogen capacity and a high heat of reaction, the metal hydride must also be able to fully absorb and/or desorb hydrogen quickly. Therefore, excellent heat transfer characteristics through the hydride forming material are essential to remove or provide the corresponding heat of reaction. Because metal hydride powders have low intrinsic thermal conductivity [9,10] (in the order of 1 W $m^{-1}$ $K^{-1}$ and less), the enhancement of the heat transfer characteristics is necessary. In this regard, plenty of suggestions can be found in the literature [9,11–15]. One of the possible solutions is to mix the hydride forming metal powder with expanded natural graphite (ENG) and fabricate composites from these mixtures. This pathway has been studied for high temperature metal hydrides in recent literature [10,16–18]. Using Hydralloy® C5, a Ti–Mn-base alloy, Pohlmann et al. [19–21] introduced stable compacted metal hydride composites (MHC) with high thermal conductivity for low temperature materials. In this case, the ENG forms a matrix within the MHC, thus, enhancing the thermal conductivity and ensuring sufficient gas permeability at the same time. Furthermore, it is assumed that the percolated ENG network stabilizes the whole MHC structure. The compaction of hydride forming metal powders with ENG increases the thermal conductivity by more than two orders of magnitude. However, the influence of prolonged cycling on MHC stability, structure and hydrogenation performance has not yet been investigated.

Numerous papers report on the cycle stability of pure metal hydrides [22–28]. For example, Friedlmeier et al. [29] investigated an $AB_2$ material ($Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$) very similar to Hydralloy® C5 ($Ti_{0.95}Zr_{0.05}Mn_{1.55}V_{0.45}Fe_{0.09}$) used in this paper. Accordingly, no degradation was identified after 42,400 cycles. With regard to the cycle stability of MHC, however, only little data is available [30,31]. Therefore, we have performed intensive experimental studies on the cycling stability of Hydralloy® C5-based MHC with respect to hydrogenation/dehydrogenation performance as well as geometrical stability. Up to 1000 hydrogenation/dehydrogenation cycles were performed using MHC with different ENG contents. In particular, temperature response, hydrogen uptake, thermal conductivity and geometrical stability were investigated. In order to test several MHC in parallel, a specific test rig was designed and brought into operation which allows fully automatic and high-dynamic pressure-induced cycles at constant absorption and desorption pressures.

## Research setting and methods

### Hydralloy® C5-graphite composites

All MHC under investigation were fabricated using Hydralloy® C5 as hydride-forming metal alloy [19]. Hydralloy® C5 (51 wt.-% Mn, 28 wt.-% Ti, 14 wt.-% V, 3 wt.-% Fe, 3 wt.-% Zr) was purchased from GfE Metalle und Materialien GmbH. The material was delivered in granular form and was milled for 5 min under argon atmosphere. The received Hydralloy® C5 powder was thoroughly mixed with 10 ± 0.1 wt.-% ENG delivered by SGL Carbon. The metal powder-ENG blends were consolidated by uniaxial compaction at 75 MPa into cylindrical MHC with 13.5 mm in diameter and a height of approximately 6.7 mm. Thereafter, a 2 mm central hole was drilled to ensure fast gas transport in axial direction. The according residual porosity within the samples was calculated on the basis of the theoretical density of each MHC using the theoretical density of ENG of about 2.1 g $cm^{-3}$ and Hydralloy® C5 of about 6.1 g $cm^{-3}$ [19]. The radial effective thermal conductivities of selected MHC samples were examined before and after cycling via the nano flash method applying a gas tight measuring cell. The complete processing chain and analytic details are described in a previous work [32].

### Test rig

*Test rig layout*

To investigate the long-term cycle stability of MHC, a special test rig was developed and brought into operation. It enables us to control and monitor large quantities of up to the kilogram range of reaction material for extensive number of cycles which allows the investigation of complete structures, e.g. matrixes for heat transfer enhancement in metal hydride composites. Four parallel test reactors with MHC samples can be monitored regarding their hydrogenation performance, MHC sample temperature and gas uptake dynamics at the same time. In particular, the time-dependence of these values during cycling is of interest. The test rig can be operated automatized at temperature levels between 50 °C and 400 °C and at hydrogen pressures up to 100 bar. During cycling large temperature changes inside the MHC occur which are tempered using a thermal fluid connected to a thermostatic bath at constant temperature. The hydrogen gas pressure can be increased or decreased quickly (in the order of seconds), thus, high-dynamic hydrogenation-dehydrogenation tests can be conducted. A schematic layout of the test rig is depicted in Fig. 1.

The temperature development within each MHC sample is monitored using a 1 mm thermocouple of type K. The thermocouple is positioned in the middle of the MHC, as here the highest temperature gradient is expected. Furthermore, the temperature within the heat transfer fluid is measured at several positions with PT100 temperature sensors. The flow rate of the heat transfer fluid is set as high as to guarantee a constant and almost identical (±1 K) temperature for all reactors. The hydrogen pressure inside the reactors is monitored using a pressure sensor (measuring accuracy: uncertainty of measurement of ±0.6 bar, reproducibility of

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