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Composite materials of melt-spun $Mg_{90}Ni_{10}$ and graphite: Microstructural changes during cyclic hydrogenation and the impact on gas and heat transport characteristics

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ABSTRACT

It is of high technical importance to consider the loading and unloading dynamics of hydride-based hydrogen storage tanks, which are mainly influenced by the heat and gas transfer properties inside the reaction bed. In this regard, hydride-graphite composites offer improved heat transfer properties and higher volumetric storage capacities compared to commonly used powder beds.

In this contribution, we report on the cycle stability of densified hydride-graphite composites based on melt-spun $Mg_{90}Ni_{10}$. The results reveal superior heat conduction properties compared to loose $Mg_{90}Ni_{10}$ flakes. Furthermore, this work deals with the hydrogenation behavior of such composites and their evolution throughout cyclic hydrogenation. Cycles at different temperatures and hydrogen pressures were conducted. High gas permeability in radial direction and sufficient thermal conductivity in combination with a stable composite structure underline the potential of such composites for hydrogen storage applications with high un-/loading dynamics.

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Introduction

The emerging hydrogen economy demands efficient, compact and safe hydrogen storage solutions. In recent years, extensive research has been carried out on various hydrogen storage materials in order to meet the ambitious targets of the US Department of Energy (DOE) regarding hydrogen storage

density, safety, efficiency or materials costs [1]. Hydrogen storage based on MgH_2 is attractive due to its high gravimetric storage capacity of 7.6 wt.-%- H_2 as well as volumetric storage capacity of 108 g- H_2 l⁻¹ in the case of bulk MgH_2 [2–4]. Therefore, MgH_2 is being considered for commercialization because of its good cycle stability and the high abundance as well as low cost of Mg as raw material [5,6]. The reaction of hydrogen with Mg liberates a reaction enthalpy of 76 kJ mol⁻¹

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Nomenclature

p_1	internal pressure, Pa
p_2	external pressure, Pa
R	universal gas constant, $\text{J K}^{-1} \text{mol}^{-1}$
T	temperature, K
M	molar mass, g mol^{-1}
η	dynamic viscosity, Pa s
h, r_1, r_2	spatial dimensions, m
Q	mass flow, g s^{-1}
k	gas permeability, m^2
α	fitting parameter, –

at a temperature of around 300 °C [7]. Therefore, MgH_2 is also considered as thermochemical energy storage medium in thermochemical reactors for the continuous production of electricity at solar thermal power plants, where the storage of heat at the temperature level between 300 °C and 400 °C is essential [8]. However, pure MgH_2 lacks of an insufficient sorption kinetic and low thermal conductivity. Thus, the transfer of the reaction heat through the reaction zone becomes a major obstacle in view of technical hydrogen storage solutions [9].

Over the last two decades, numerous studies have been conducted to achieve an enhanced hydrogenation kinetics of Mg and its alloys. Two fundamental routes were followed: Firstly, the generation of a nano-scale microstructure of the storage material, which is usually used as powder, and, secondly, the insertion of active catalyst species with a homogeneous distribution [10–15]. Moreover, recent years have seen a revival of research activities from the late 1970's and 1980's regarding the production of hydride composite materials with an enhanced effective thermal conductivity in order to address the issue of heat transfer through the hydride bed [16–21]. Thereby, the (un-)loading dynamics of a hydride-based storage tank can be drastically improved. In principle, two options have been followed here: Firstly, auxiliary metal structures with high thermal conductivity like open-cellular nickel or aluminum foams into which hydride particles are inserted [22,23]. Secondly, hydride-graphite composites have been prepared [24–28]. The latter method allows a standard powder mixing process and to tailor the thermal conductivity very accurately and to create even anisotropic heat conduction properties which can be beneficial for tubular storage vessel geometries [26,27].

In our previous works, melt spinning was employed to produce ultra-fine microstructures of Mg–Ni and Mg–Ni–Y alloys suitable for hydrogen storage with reversible gravimetric storage capacities of up to 5.5 wt.-%- H_2 and hydrogen uptake rates of up to 1.3 wt.-%- H_2 per minute [29,30]. Since Ni is well known to show a strong catalytic effect upon hydrogenation of Mg through the formation of the Mg_2Ni phase and its hydrides [2,31–33], in this work a melt-spun Mg–Ni alloy ($\text{Mg}_{90}\text{Ni}_{10}$) is used as starting material to produce $\text{Mg}_{90}\text{Ni}_{10}$ -graphite composites using expanded natural graphite (ENG), in particular. As shown in our previous works, solid bodies (cylindrical pellets) which were prepared by densification of the powdery material blend can be tailored concerning their effective heat conduction property, their phase alignment and

their volume fraction of residual porosity [27,34]. In this regard, the radial thermal conductivity of cylindrical $\text{Mg}_{90}\text{Ni}_{10}$ -ENG compacts can be increased up to $47 \text{ W m}^{-1} \text{ K}^{-1}$. This is very beneficial considering a cylindrical geometry of the storage container where the reaction enthalpies have to be transported in radial direction, preferably. In order to reach acceptable hydrogen loading times in the range of 1 wt.-%- H_2 per minute, the effective heat conductivity within the hydrogen storage material should be in the range from 10 to $20 \text{ W m}^{-1} \text{ K}^{-1}$ in radial direction [27]. In order to meet this target range, suitable processing and materials parameters were chosen.

This contribution deals with the long-term stability of suchlike prepared $\text{Mg}_{90}\text{Ni}_{10}$ -ENG compacts which are examined concerning their hydrogenation behavior. $\text{Mg}_{90}\text{Ni}_{10}$ -ENG composites with a ENG content of 10 wt.% (compacted at 300 MPa) were repeatedly hydrogenated and dehydrogenated. In principle, three states are of technical interest: the $\text{Mg}_{90}\text{Ni}_{10}$ -ENG composite in (a) the as-compacted state, (b) after cyclic hydrogenation in the hydrogenated and (c) after cyclic hydrogenation in the dehydrogenated state. At these three states, thermal conductivity, gas permeability and phase alignment (microstructure) were systematically investigated for different cycle numbers in order to deduce the suitability of these composites as stable hydrogen storage materials.

Experimental

In this study, nanocrystalline Mg–Ni alloy flakes were prepared by melt spinning and subsequent chopping. For this purpose, $\text{Mg}_{90}\text{Ni}_{10}$ master alloy ingots were produced by induction melting of a mixture of pure Mg metal (99.9% purity) and Ni powder (99.9% purity) in a tantalum crucible under argon atmosphere. Melt spinning of this master alloy was then carried out under argon atmosphere. The resulting $\text{Mg}_{90}\text{Ni}_{10}$ ribbons were between 40 μm and 80 μm in thickness and 10 mm in width (cf [27]). X-ray diffraction (XRD, Bruker AXS: D8 ADVANCE) using $\text{Cu K}\alpha$ radiation in the angular range between 20° and 60° (2θ) was performed on the as-spun ribbons to judge their degree of crystallinity. For further materials manufacturing, a powder metallurgical technology chain was followed. The melt-spun $\text{Mg}_{90}\text{Ni}_{10}$ ribbons were repeatedly chopped (Retsch SM 2000) into flakes until a maximum lateral flake size of about one millimeter was obtained. Yet, a broad lateral flake size distribution is examined (cf [27]). Thereafter, the $\text{Mg}_{90}\text{Ni}_{10}$ flakes were thoroughly mixed with 10 wt.% ENG (delivered by SGL Carbon) in a tubular mixer. The ENG is of high purity (highest amounts of impurities: $\text{Fe} < 150 \text{ ppm}$ and $\text{Si} < 100 \text{ ppm}$) and not pretreated in any way in the as-delivered state. Formerly, we had measured a radial thermal conductivity of about $370 \text{ W m}^{-1} \text{ K}^{-1}$ of pure ENG pellets [27]. After mixing, the $\text{Mg}_{90}\text{Ni}_{10}$ -ENG blend was consolidated by uniaxial compaction (TIRA test 2300) at 300 MPa into composites (cylindrical pellets) with 14 mm in diameter and several ten millimeters in height. Those processing parameters were obtained from our previous works to accomplish Mg–ENG composites with a residual porosity of about 35 vol.%. For comparison a set of pelletized $\text{Mg}_{90}\text{Ni}_{10}$

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