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Hydrogen storage properties of compacts of melt-spun $Mg_{90}Ni_{10}$ flakes and expanded natural graphite

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ABSTRACT

In recent years, melt-spun magnesium alloys have attracted a lot of attention due to their excellent (de-)hydrogenation characteristics resulting from their nanoscale crystal structure and the homogeneous distribution of minor catalyst phases. Besides reaction kinetics, the heat conductivity of the storage material is important to transfer the reaction enthalpies in a controlled manner. Due to the inferior heat conduction properties of magnesium hydride, composites containing melt-spun $Mg_{90}Ni_{10}$ flakes and expanded natural graphite (ENG) up to 25.5 wt.% have been examined. Mixtures of those starting materials were compacted to cylindrical pellets using compaction pressures up to 600 MPa. Investigations of thermal conductivities in radial and axial directions, microstructure and phase fractions were carried out upon all sets of specimens. The heat transfer characteristics were tuned in a wide range from 1 up to 47 $W\,m^{-1}\,K^{-1}$. Furthermore, cyclic (de-)hydrogenation was carried out upon the compacts showing a hydrogen uptake of up to 4 wt.%-H_2 within 10 min. During the hydrogen loading process, the $Mg_{90}Ni_{10}$–ENG pellets remained mechanically stable.

1. Introduction

In recent years, the (de-)hydrogenation kinetics of magnesium-based systems have been enhanced steadily by producing nano-scale microstructures and by adding catalytically active constituents (e.g. transition metals, metal oxides, rare earth elements or carbon-based additives) [1–5]. Another approach considering hydride-based hydrogen storage systems is the improvement of the heat transfer characteristics of the commonly granular hydrogen storage material, especially in its hydrogenated state. Thereby, the storage tank's (un-)loading dynamics can be controlled, too. A few studies were conducted to improve the rather poor thermal conductivity of MgH_2 of less than 1 $W\,m^{-1}\,K^{-1}$, which can be divided into two groups: At first, supplementary metallic structures were used with high thermal conductivity like nickel or aluminium foams [6–8]. Secondly, the preparation of hydride–graphite composites was pursued with increased effective thermal conductivity [9–12]. Accurate tailoring of the thermal conductivity and creating anisotropic heat conduction properties can be achieved by the latter method. For example, Chaise et al. [9] increased the effective thermal conductivity of compacts of magnesium hydride and 10 wt.% expanded natural graphite (ENG) to about 8 $W\,m^{-1}\,K^{-1}$ in the direction of ENG alignment.

As demonstrated in our previous publications, melt spinning allows to produce nanoscale microstructures of Mg–Ni and Mg–Ni–Y alloys with gravimetric hydrogen storage capacities of up to 5.5 wt.%-H_2 and hydrogen uptake rates of up to 1.3 wt.%-H_2 per minute [13,14]. Considering the well known catalytic effect of Nickel upon hydrogenation of magnesium [15–17], a melt-spun magnesium–nickel alloy ($Mg_{90}Ni_{10}$) is used in this work as starting material to produce $Mg_{90}Ni_{10}$–ENG composites with ENG contents of up to 25.5 wt.%. Furthermore, the tank architecture sets essential requirements upon the heat flux inside the storage material. In this regard, a reasonable design, which can be found in various publications [8,18–21], is a cylindrical geometry where the heat flux needs to be transported only in radial direction. 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 $W\,m^{-1}\,K^{-1}$ in radial direction according to our approximate calculations.

In this contribution, it is demonstrated that the radial thermal conductivity of cylindrical $Mg_{90}Ni_{10}$–ENG compacts can be tailored in a wide range. Further, it is shown for the first time that the compacts can be hydrogenated while keeping their mechanical sta-

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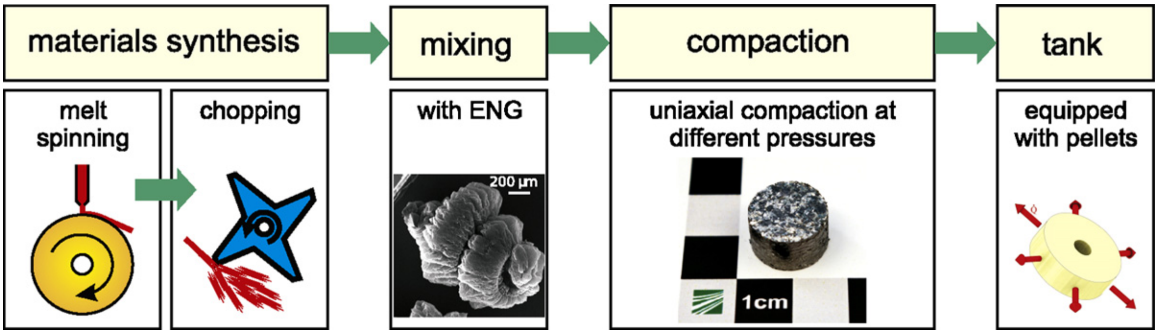

Fig. 1. Schematic technology chain of the production of melt-spun magnesium–ENG compacts.

bility. Additionally, we present a technology chain which shows the technical feasibility of the production of the hydride–graphite pellets which are to be used in the cylindrical tank system.

2. Experimental

The initial metallic state of $Mg_{90}Ni_{10}$ was prepared by melt spinning. For this purpose, $Mg_{90}Ni_{10}$ 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 $Mg_{90}Ni_{10}$ ribbons were 40 µm in thickness and 10 mm in width (cf. [13]).

For further materials manufacturing, a powder metallurgical technology chain was followed, which schematically is depicted in Fig. 1. The melt-spun $Mg_{90}Ni_{10}$ ribbons were repeatedly chopped (Retsch SM 2000) until a maximum flake size of about 1 mm was reached. Afterwards, mixtures of $Mg_{90}Ni_{10}$ flakes with three different ENG (delivered by SGL Carbon) contents of 5.0, 10.0 and 25.5 wt.% were produced using a tubular mixer. After mixing, the $Mg_{90}Ni_{10}$–ENG blend was consolidated by uniaxial compaction (TIRA test 2300) into cylindrical pellets with 14 mm in diameter. Three different compaction pressures, 150, 300 and 600 MPa, were applied. A future tank construction can be equipped with similar prepared pellets which can be larger in diameter and possibly ring shaped.

The geometric density of the pellets was determined. Thereby, the residual porosity within the specimen was calculated by comparison of the pellets' densities with their theoretical bulk densities. The densities of the bulk materials were measured with a pycnometer on single phase pellets (AccuPyc 1330). Inaccuracies of the weight measurements conducted are negligibly small since the systematic error of the used microbalance is less than 0.05 mg. Concerning the measurements of the pellet dimensions (diameter, height), the error of the micrometer caliper employed amounts to 0.004 mm.

In order to distinguish the thermal conductivity in axial and radial direction, the pellets were cut into two 2 mm thin slices (using an Accutom 5), which were orientated parallel and perpendicular to the direction of compression. The slices were examined using the flash method (Netzsch LFA 447 NanoFlash) determining temperature diffusivity with an uncertainty of 3% (value given by the manufacturer). The corresponding thermal conductivity was calculated by multiplying temperature diffusivity, density and specific heat capacity. The specific heat capacity was determined using the DSC method (Netzsch DSC 204 F1 Phoenix) with an uncertainty of 3% (value given by the manufacturer). The summation of the major measurement errors results in an uncertainty of about 10% for the thermal conductivities stated. Furthermore, axial and radial cross-sections of each specimen were prepared for metallographic examination (optical and scanning electron microscopy (SEM)).

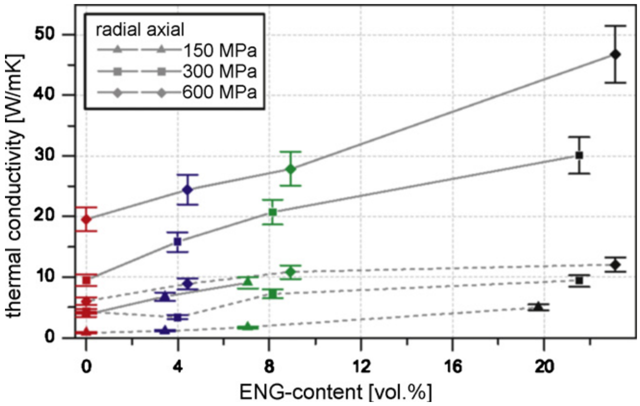

Fig. 2. Radial (solid line) and axial (dashed line) thermal conductivities of the $Mg_{90}Ni_{10}$–ENG compacts at compaction pressures of 150, 300 and 600 MPa vs. ENG content (0 wt.% red, 5 wt.% blue, 10 wt.% green, 25.5 wt.% black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In order to investigate the stability of the $Mg_{90}Ni_{10}$–ENG pellets during cyclic (de-)hydrogenation, a pellet was placed in a special container in order to set geometrical constraints as it would be the case in a realistic tank (cf. inclusion in Fig. 4). The measurement was performed by thermogravimetry (TG) using a magnetic suspension balance (Rubotherm). The thermal activation of the pellet was achieved during three cycles at 385 °C and pressures between 2 and 30 bar H_2 (99.9998% purity) for 10 h.

3. Results and discussion

As demonstrated in our previous work, the mean porosities of $Mg_{90}Ni_{10}$–ENG pellets are decreasing with increasing compaction pressure [22]. The porosity is reduced with increased ENG content leading to a good compactibility due to the fact that ENG acts as lubricant. The porosity within the $Mg_{90}Ni_{10}$–ENG pellets can be

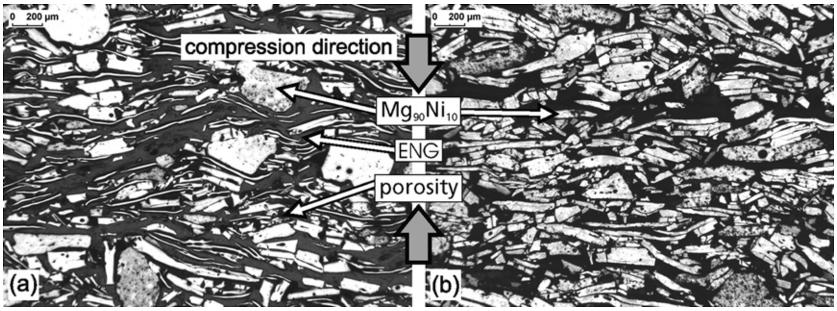

Fig. 3. Optical micrographs of the $Mg_{90}Ni_{10}$–ENG compacts containing (a) 25.5 wt.% and (b) 5.0 wt.% ENG both compacted at 150 MPa (arrows indicating compression direction).