



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Hydrogen storage and thermal transport properties of pelletized porous Mg-2 wt.% multiwall carbon nanotubes and Mg-2 wt.% graphite composites

L. Popilevsky^{a,b}, V.M. Skripnyuk^a, M. Beregovsky^a, M. Sezen^c,
Y. Amouyal^a, E. Rabkin^{a,*}

^a Department of Materials Science and Engineering, Technion–Israel Institute of Technology, 32000 Haifa, Israel

^b Grand Technion Energy Program (GTEP), Technion–Israel Institute of Technology, 32000 Haifa, Israel

^c Nanotechnology Research and Application Center (SUNUM), Sabanci University, Orhanli, Tuzla, 34956 Istanbul, Turkey

ARTICLE INFO

Article history:

Received 3 December 2015

Received in revised form

16 February 2016

Accepted 1 March 2016

Available online xxx

Keywords:

Magnesium hydride

Multiwall carbon nanotubes

High energy ball milling

Porous metal matrix composites

ABSTRACT

We synthesized pelletized porous composites of Mg admixed with 2 wt.% of either multiwall carbon nanotubes or graphite. The composites were prepared by high energy ball-milling of Mg powder with carbonaceous additives, followed by uniaxial compression and sintering in hydrogen environment under mechanical constraint. The correlations between ball-milling conditions, composite microstructure, hydrogenation kinetics, and thermal conductivity of the pellets were established. The presence and condition of carbon additives controls the morphology of Mg particles and, consequently, the mechanical stability of the pellet upon hydrogenation cycling. The best combination of hydrogen desorption kinetics, thermal conductivity, and mechanical stability was obtained for the pellets synthesized from the mixture of Mg with 2 wt.% of carbon nanotubes processed by 4 h of co-milling. The milling transformed carbon nanotubes into carbon nano-particles/nano-onions. These carbonaceous species promote metal nucleation from the hydride phase and allow formation of Mg-Mg bonds between the Mg particles contributing to mechanical stability of the pellet.

Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Magnesium is considered as one of the most attractive materials for hydrogen storage because of its high hydrogen storage capacity and abundance. However, its main drawbacks are slow hydrogenation kinetics and high formation enthalpy of MgH₂ hydride. Ball-milling of Mg powders was

shown to reduce crystallite and particle size, break the surface oxide layer, introduce defects and activate the surface for hydrogen absorption [1]. As a result, the hydrogenation kinetics of Mg-based powders can be accelerated. In materials with high hydride formation enthalpy, hydrogen absorption reaction is highly exothermic. For the hydrogenation reaction to proceed, the heat should be quickly removed, while for the

* Corresponding author. Tel.: +972 4 829 4579; fax: +972 4 8295677.

E-mail address: erabkin@tx.technion.ac.il (E. Rabkin).

<http://dx.doi.org/10.1016/j.ijhydene.2016.03.014>

0360-3199/Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

endothermic desorption process, the heat supply is crucial. Thus, the ability of the hydride-forming metal to conduct heat often represents the kinetic “bottleneck” determining the hydrogenation kinetics. Unfortunately, thermal conductivity of powder beds is very low due to their high surface to volume ratio and poor contact between individual particles.

Compacting the powders into the porous pellet form along with addition of materials with high thermal conductivity improves thermal conductivity of the composite and simplifies the design and assembly of hydrogen storage tank. Ron [2,3] was the first to produce solid porous pellets with excellent hydrogenation properties. According to the proposed method, the mixture of the powders of LaNi₅ hydride and of Al (high thermal conductivity additive) was firstly consolidated into the pellets form using uniaxial pressure at room temperature. In the next step, the consolidated pellets were sintered in a special fixture preventing the volume expansion of the pellet, under hydrogen pressure exceeding the equilibrium plateau pressure at the sintering temperature. These sintered pellets exhibited high thermal conductivity, fast hydrogenation kinetics, and good cycling stability. The disadvantage of this method is that Al acts only as a highly heat-conducting binder between hydride forming particles since it does not form stable hydrides in the course of hydrogenation, does not possess catalytic properties, and also reduces the hydrogen storage capacity of the composite. In the presented work magnesium-hydride-based composites were manufactured based on the method described above, and employing carbon-based additives exhibiting high catalytic activity which accelerates the hydrogenation kinetics. The positive effect of carbonaceous additives on hydrogenation properties of pelletized magnesium-hydride-based composites has been demonstrated in several previous works [4–6]. It was shown that both the thermal conductivity and mechanical stability during hydrogenation cycling of the compacted pellets can be significantly improved by a proper choice of the uniaxial compaction pressures and of the content of carbonaceous additive.

Several groups reported that hydrogenation properties of Mg-based alloys can be improved by carbonaceous additives, such as carbon nanotubes (CNTs) [7,8] and graphite [8,9]. The CNTs are known for their exceptional chemical and thermal stability and excellent electrical and thermal conductivity [9–11]. Kim et al. [10] have reported that maximum thermal conductivity of individual multi-wall carbon nanotubes (MWCNTs) at ambient temperature is about 3000 W/mK, which is higher than that of a single crystal diamond. However, mass-produced carbon nanotubes are randomly oriented/entangled inside the agglomerates. Numerous junctions between the nanotube segments inside these agglomerates turn the latter into thermal insulator [11]. Thus, for improving thermal conductivity these agglomerates have to be dispersed. Ball-milling is a mature materials processing method that can easily tune morphologies and properties of carbonaceous materials. By varying the milling parameters such as rotation speed, balls-to-powder weight ratio, and milling time, closed multi-wall carbon nanotubes (MWCNTs) can be transformed into short, open-ended tubes [12,13]. It was shown by Pierard et al. [13] that MWCNTs break at the sites with highest curvature. Li et al. suggested a route for

the formation of carbon nano-onions from MWCNTs during high-energy ball-milling [12]. CNT failure begins from collapse at the defective sites, such as bent or curved sections. Further milling can lead to the walls collapse at the nearby location; the subsequent walls closure results in formation of elliptic carbon nano-particles evolving into chemically stable spherical carbon onions [14]. Milling for long times may also transform CNTs into graphite with its usual layered structure, mixed with amorphous regions [15]. Significant amorphization was observed as well. It was demonstrated that defects introduced by ball milling have a positive effect on catalytic activity of MWCNTs. For example, Chen et al. [7] reported that highly damaged MWCNTs are surrounded by larger amount of Mg and MgH₂ crystals as compared to the defect-free straight MWCNT segments.

Graphite is a material formed by stacking of single graphene layers. Each layer is a strong sp² carbon hexagonal network, while the layers interact with each other by weak van der Waals forces. In-plane thermal conductivity of highly ordered pyrolytic graphite can reach up to 2000 W/mK [16]. However, weak interaction forces in the out-of-plane direction of graphite are responsible for the decrease in the thermal conductivity by two orders of magnitude in this direction. Among the defects that were reported to be produced during graphite ball-milling are delamination in the in-plane direction, formation of graphene nano-sheets [17] and their warping in graphene sheets [18], formation of closed-shell nanostructures [19], stacking disorder in the axial direction [20], curling into carbon nanotubes [21] and amorphization resulting in a random mixture of sp³, sp² and sp¹ bonds [22]. Bouaricha et al. [23] have reported that addition of graphite to Mg during ball-milling prevents formation of oxide layers that can slow down hydrogen diffusion, and reduces final crystallite size. It was shown by Imamura et al. [24] that when Mg and graphite were milled in the presence of organic solvent, delamination and cleavage of graphite in the in-plane direction resulted in enhancement of hydrogenation kinetics due to charge transfer between the Mg particles and graphite flakes. On the contrary, when ball-milling was performed without addition of solvent, irregularly broken amorphous graphite did not result in any improvement of hydrogenation kinetics.

In this work we synthesized porous pellets of Mg admixed with either 2 wt. % of MWCNTs or 2 wt. % of graphite. We studied the influence of ball-milling parameters on the obtained morphology, hydrogenation kinetics and thermal conductivity of the porous pellets. We will demonstrate that proper selection of the milling conditions allows producing mechanically stable solid porous Mg-carbon pelletized composite with improved hydrogenation kinetics, while minimizing thermal conductivity loss.

Experimental

As-cast Mg of commercial purity was used. Mg chips with the sizes of up to 1 mm were obtained by comminuting with file. MWCNTs were supplied by Cheaptubes, Inc. (Outer diameter is in the range of 20–30 nm, length is in the range of 10–30 μm, purity: >95%, true and bulk density of 2.1 g/cm³ and 0.28 g/

Download English Version:

<https://daneshyari.com/en/article/7709925>

Download Persian Version:

<https://daneshyari.com/article/7709925>

[Daneshyari.com](https://daneshyari.com)