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Effect of ball-milling duration and dehydrogenation on the morphology, microstructure and catalyst dispersion in Ni-catalyzed MgH_2 hydrogen storage materials

Stephen D. House,[a,*,1] John J. Vajo,[b] Chai Ren,[c] Angus A. Rockett[a] and Ian M. Robertson[a,d]

[a] *Department of Materials Science, University of Illinois at Urbana-Champaign, 1304 W. Green St., Urbana, IL 61801, USA*
[b] *HRL Laboratories, LLC, 3011 Malibu Canyon Road, Malibu, CA 90265, USA*
[c] *Department of Metallurgical Engineering, University of Utah, 135 S. 1460 E, Salt Lake City, UT 84112, USA*
[d] *Department of Materials Science and Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, USA*

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Abstract—The effects of high-energy ball-milling on catalyst morphology and dispersion as a function of milling duration and on hydrogen desorption were investigated. Samples of MgH_2 doped with 0.05 Ni catalyst were examined after 1, 5 and 10 h of milling. Longer milling durations produced finer catalyst particle sizes and more uniform dispersions, but yielded higher hydrogen desorption temperatures. This behavior is attributed to the formation of Mg_2NiH_4 with increased milling times. Electron tomography was used to show that the Ni particles reside both inside and outside the MgH_2 particles. On dehydrogenation there was a redistribution of catalyst and continued formation of Mg_2Ni. The formation of this phase is proposed to explain the reported degradation of hydrogen capacity and the change in kinetics of this system with cycling.

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1. Introduction

The requirements of developing a light-weight onboard regenerative hydrogen storage system for H_2-powered fuel cell automobiles pose a significant challenge [1]. The high gravimetric and volumetric densities of complex metal hydrides based on light metals – such as Li, Na, Mg, Ca and Al – make them attractive candidate materials for storage [2–5]. Magnesium hydride has garnered attention both for its gravimetric (7.6 wt.%) and volumetric ($110\ g\ l^{-1}$) hydrogen storage densities and for the fact that it is abundant, relatively inexpensive and non-toxic. The thermodynamic stability of MgH_2, however, means that a high temperature of 350–400 °C is required for hydrogen desorption and its kinetics are sluggish, requiring a temperature above 300 °C and a pressure of ~20 bar to hydrogenate [6–11].

Nanocrystalline MgH_2 produced by high-energy ball-milling exhibits faster absorption and desorption kinetics, without the need for activation cycles, than bulk or larger-grained polycrystalline Mg [12–15]. These enhancements from mechanical milling are attributed to the reduction in particle size, which decreases the diffusion distance for hydrogen [16]; the increase in specific surface area [17]; and the formation of defects. High-energy ball-milling has the added benefit of being a relatively simple process, and thus has become the primary method for producing many hydride materials for hydrogen storage. Although ball-milling alone is insufficient to reach the performance targets [18,19], the sorption temperatures and kinetics can be further improved by the addition of various catalysts, primarily transition metals (e.g. Ti, Fe, Ni, Nb, V) [20–22], transition metal oxides (e.g. Nb_2O_5, Cr_2O_3) [19,23,24] and intermetallic compounds (e.g. FeTi, $LaNi_5$, $TiMn_2$) [25–27].

The effectiveness of Ni catalyst at enhancing the kinetics of Mg/MgH_2 has been well established [8,9,28,29]. In a systematic study of Ni-doped Mg powders, Bogdanović et al. showed reasonable cyclic stability, but noted a drop in hydrogen capacity with cycling relative to bulk Mg, particularly at higher temperatures [9]. In studying Ni-plated Mg films, Eisenberg et al. observed degradation in the hydrogen

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[*] Corresponding author. Tel.: +1 847 250 7357; e-mail: sdh46@pitt.edu

[1] Present address: Department of Chemical and Petroleum Engineering, University of Pittsburgh, 3700 O'Hara St, Pittsburgh, PA 15261, USA.

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sorption rates with cycling, and suggested that the amount of surface Ni in contact with the Mg was important [28]. This degradation in capacity and sorption kinetics was also reported by Hanada et al., who, additionally, noted an increase in the hydrogen desorption temperatures with increasing milling duration as early as the second cycle [22].

Experimental and computational studies have indicated that the location of the catalytic additives – e.g. on the surface, at interfaces or inside the particles; well-dispersed or agglomerated – determine their ability to enhance the hydrogen sorption kinetics of magnesium and magnesium hydride [30–33]. The small amount of catalyst required, typically a few at.%, makes it all the more important to know where the catalyst resides initially and after hydrogen cycling. Although there have been efforts to identify the location of the catalyst, the results have been ambiguous [12,22,34–39].

In this paper, the effect of high-energy ball milling duration and hydrogen desorption on the morphology, microstructure and catalyst dispersion of the $MgH_2 + 0.05$ Ni system is presented. The effect of milling time is investigated using a combination of characterization techniques, including electron microscopy, tomography and diffraction; energy-dispersive X-ray spectroscopy (EDX); and X-ray diffraction (XRD). The effect of dehydrogenation on the catalyst dispersion and form is explored via in situ scanning transmission electron microscopy (STEM) heating experiments. The results have implications regarding the performance degradation of this system.

2. Experimental

The storage material used in this work was prepared from magnesium hydride (MgH_2, 95% purity) and Ni nanopowder (50 nm average diameter) obtained from Gelest and Argonide Corp., respectively. Examination of the Ni nanopowder found it to consist of spherical particles 10–80 nm in diameter. Mixtures of MgH_2 and Ni at a 20:1 ratio were milled in a Pulversette 6 planetary mill from Fritsch using an 80 cm^3 hardened steel milling vessel and 30 chrome-steel 7 mm diameter milling balls. Approximately 1 g of each mixture was milled at 400 rpm under an argon gas environment. Three batches were prepared, which were milled for a range of durations: 1, 5 and 10 h. All sample handling during preparation was performed in an argon-filled glovebox with O_2 and H_2O concentrations <1 ppm.

The hydrogen release properties of the storage material were evaluated using a Shimadzu TGA-50 thermogravimetric analyzer (TGA) mounted inside a glovebox with O_2 and H_2O levels <0.5 ppm. Powder, 17–20 mg, was placed inside a platinum crucible and heated under 50 ml min^{-1} flowing argon gas. The TGA was programmed to heat the specimen at a rate of 5 °C min^{-1} up to a maximum temperature of 550 °C.

Powder XRD was performed on the as-milled material using a Siemens-Bruker D-5000 X-ray diffractometer with monochromated Cu Kα ($\lambda = 0.15418$ nm) X-rays. A low-background quartz sample holder with a recessed circular cavity, 8 mm in diameter and 1 mm in depth, was loaded with powder inside the Ar-atmosphere glovebox. Kapton tape, 3.175 cm wide, was placed over the cavity to protect the powder from exposure to oxygen and moisture during transfer and data acquisition. Spectra were acquired over the angular range $2\theta = 20–80°$ at a step size of 0.02° and scan speed of 0.25° min^{-1}. Total scan time was 4 h. No noticeable difference in powder color was observed over the course of the scans, with only a slight release of gas some time after 2 h, though the Kapton tape remained airtight.

The morphological and microstructural characterization of the materials was performed using transmission electron microscopy (TEM) for imaging, selected area electron diffraction (SAED) and in situ heating experiments; STEM for imaging, EDS for compositional analysis, and in situ heating experiments; and scanning electron microscopy (SEM) for surface imaging. The primary TEM used was a JEOL 2010 TEM equipped with a LaB_6 thermionic source. The primary STEM used was a JEOL 2010F S/TEM equipped with a Schottky field-emission source and an Oxford Instruments atmospheric thin window energy-dispersive X-ray spectrometer. STEM tomography and additional EDS on the 1 h milled specimen was performed using an FEI Tecnai F20ST S/TEM equipped with a Schottky field-emission source and an EDAX Sapphire Si(Li) ultra-thin window energy-dispersive spectrometer. All STEM analyses were performed at an operating voltage of 200 keV. The SEM used was a JEOL 7000F SEM, equipped with a Schottky field-emission source and operated at 15 keV.

Only the MgH_2 exhibited any noticeable changes during STEM observation: contrast fluctuations, small void formation and the appearance of Mg diffraction spots in SAED patterns. These changes occurred well within 1 min of exposure, after which the material stabilized, and no further changes were observed. This indicates that the effect of beam exposure was beam-heating-induced decomposition of MgH_2 to Mg. The Ni catalyst particles did not change in size, shape or location, even if the surrounding MgH_2 was affected. It was found that operating at magnifications less than $\times 10^5$ in the STEM and with the beam defocused in the conventional TEM yielded negligible damage due to the beam beyond the initial heating. The effect of prolonged beam exposure, such as experienced during EDS and acquisition of the images for electron tomography, is discussed further in Fig. S.0 in Supporting Information. To ensure that the phenomena observed in the tracked particles during the heating experiments were not merely the result of beam effects, new particles, which had not been previously imaged or scanned, were examined after each heating step. No significant differences in their morphological evolution were noted between the tracked and new particles.

Specimens for microscopy were prepared by applying the powdered material to holey carbon coated Cu TEM grids (SPI supplies) inside a MBraun argon-filled glovebox maintained at O_2 and H_2O concentrations <0.1 ppm. To minimize exposure to the environment during the TEM and STEM experiments on the JEOL instruments, a Gatan HHST 4004 environmental vacuum cell transfer stage was utilized. The grids were loaded into the stage inside the glovebox. Then the stage tip was retracted into the vacuum cell where it was sealed and evacuated to a roughing vacuum pump level, after which it was inserted into the microscope column. The samples examined in the Tecnai F20 were mounted in a Model 1000F single-tilt tomography holder from Hummingbird Scientific and were exposed briefly to atmosphere during transfer from the glovebox to the microscope. The samples examined in the SEM, mounted on an aluminum stub, were likewise briefly

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