Effect of ball-milling duration and dehydrogenation on the morphology, microstructure, and catalyst dispersion in Ni-catalyzed MgH₂ hydrogen storage materials

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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 MgH₂ doped with 0.05 Ni catalyst were examined after 1, 5, and 10 hours 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 Mg₂NiH₄ with increased milling times. Electron tomography was used to show that the Ni particles reside both inside and outside the MgH₂ particles. On dehydrogenation there was a redistribution of catalyst and continued formation of Mg₂Ni. 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.

Keywords: Electron Hydrogen-storage materials, Complex hydrides, *In situ* transmission electron microscopy (TEM), STEM HAADF, Electron Tomography

1. Introduction

The requirements of developing a light-weight onboard regenerative hydrogen storage system for H₂-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) hydrogen storage densities and the fact that it is abundant, relatively inexpensive, and non-toxic. The thermodynamic stability of MgH_2 , however, means a high temperature of 350-400 °C is required for hydrogen desorption and its kinetics are sluggish, requiring a temperature above 300 °C and pressure around 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 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 atomic percent, 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 article, the effect of high-energy ball milling duration and hydrogen desorption on the morphology, microstructure, and catalyst dispersion of the $\text{MgH}_2 + 0.05 \text{ Ni}$ 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; and X-ray diffraction. The effect of dehydrogenation on the catalyst dispersion and form is explored via *in situ* S/TEM 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 cm³ 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 hours. 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 flowing argon gas. The TGA was programmed to heat the specimen at a rate of 5 °C/min up to a maximum temperature of 550 °C.

Powder x-ray diffraction (XRD) was performed on the as-milled material using a Siemens-Bruker D-5000 x-ray diffractometer with monochromated Cu K α ($\lambda = 0.15418 \text{ nm}$) 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. Total scan time was 4 hours. No noticeable difference in powder color was observed over the course of the scans, with only a slight release of gas sometime after 2 hours, 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; scanning transmission electron microscopy (STEM) for imaging, energy-dispersive x-ray spectrometry (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 LaB₆ 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-hour 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 S/TEM analysis was 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 MgH₂ exhibited any noticeable changes during S/TEM observation: contrast fluctuations, small void formation, and the appearance of Mg diffraction spots in SAED patterns. These changes occurred well within a minute 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 MgH₂ to Mg. The Ni catalyst particles did not change in size, shape, or location even if the surrounding MgH₂ was affected. It was found that operating at magnifications < 100 kX in the STEM and with the beam defocused in CTEM 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 Figure S0 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 O₂ and H₂O 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 exposed to atmosphere. In both cases, exposure was typically less than 10 minutes.

The *in situ* TEM and STEM heating experiments were performed using the vacuum transfer stage. While inserted into the microscope, the specimens were heated to 300 °C at a rate of 5-6 °C/min, held for 25 minutes, then cooled at a rate of about 10 °C/min. The temperature reported is the nominal temperature; the actual temperature of the material is not known because other than the copper grid, the material is not in direct contact with the heating element. During observation prior to heating, the locations of selected particles were recorded to allow for reexamination after the subsequent heating steps. In addition to tracking specific particles, additional particles were examined after each heating increment.

The alignment and reconstruction for electron tomography was performed using EM3D [40], which implements a weighted back-projection algorithm. UCSF Chimera [41] and ImageJ [42] were used for visualization and analysis of the tomogram.

3. Results

3.1 Dehydrogenation Performance of Ni-catalyzed MgH₂

The hydrogen release behavior of the samples is shown in Figure 1a as the fractional weight loss curves for dehydrogenation and in Figure 1b as the derivative weight loss (wt%/°C); the onset temperature for hydrogen release and the final weight % loss are listed in Table 1. The dehydrogenation performance degraded with increased mechanical milling duration, although this appears to plateau. The 1-hour specimen exhibited a roughly 25 °C lower desorption

temperature than the 5- and 10-hour specimens, which had effectively identical onset temperatures. Dehydrogenation appeared to complete at about the same temperature, with the 1- and 10-hour specimens both having released 5.9 wt% of hydrogen by 325 °C. A second set of samples were dehydrogenated, the results of which are given in parentheses in Table 1; they exhibited the same trends. The desorption data in Figure 1b were quantitatively analyzed by fitting the curves as multiple thermally stimulated desorption processes. A detailed description of this procedure, and the resulting fits, are included in the Supporting Information, Figures S3-S5. The peak positions and fitting parameters are listed in Table 2. The fitting suggests that for each sample there are two to three desorption processes with activation energies on the order of 1.8 ± 0.1 eV. The sudden decrease in desorption rate on the high temperature side of the peaks places a lower bound on the activation energies. The onset of desorption in the 1-hr milled specimen is gradual, and is likely a continuously increasing activation energy and so this portion was not fitted with a peak. The onset sharpens dramatically as milling duration increased with the 10-hr milled specimen showing the fastest dehydrogenation rate. Most of the desorption in the 1-hr specimen occurs in the 255 ± 5 °C peak, while for longer milling times an increasing fraction of the total desorption occurs in the higher-temperature peaks. After 10 hours of milling, almost all the desorption occurred in the 270 ± 5 °C peak. The component that peaks at 295 ± 5 °C is somewhat stronger in the sample milled for 5 hours, but the fit cannot give a unique trend in this component with the limited data available. The 5-hr milled material also yielded a more complex desorption behavior with more peaks than the 1- and 10-hr material.

3.2 Morphology and Catalyst Dispersion as a Function of Milling Time

The indexed powder XRD spectra acquired from the 1- and 10-hour-milled material, along with the Kapton tape background spectrum, are shown in Figure 2. The diffraction peaks were analyzed using MDI JADE, which confirmed the presence of all the expected diffraction peaks for MgH_2 and Ni in the acquisition range. The MgH_2 peaks most closely correspond to those of the $\alpha\text{-MgH}_2$ phase. The MgH_2 peaks of the 10-hour specimen are broader and less intense than in the 1-hour specimen, supporting the refinement of grain size with milling. Select diffraction peaks of the MgH_2 and Ni from the 1-hour- and 10-hour-milled samples were enlarged for further examination and are presented in Figure 3. Each of the MgH_2 peaks of the 1-hour material exhibited doublet peaks located to the right of the main peaks. The spacing of these

doublets was too large to be due to K_{α} - K_{β} splitting. These doublets were fitted using OriginPro, (cf. Figure S6 in SI, and Table 3). The crystal lattice associated with these peaks is the same as for the main peaks but with a contraction of $\sim 1\%$. Peak heights and areas were also extracted from the fits and these data are presented in Table 4. From the total area, the mass ratio of the two phases associated with the main and doublet peaks was ~ 1.52 for five MgH_2 peaks. Doublet peaks could not be distinguished in the XRD spectra of the 10-hour milled material, however, the MgH_2 peaks are broad enough and positioned such that the doublet peak may be obscured by the main peak.

Comparing the Ni peaks, Figure 3b, in the 1-hr and 10-hr milled samples suggests a decrease in the particle size and the formation of the intermetallic Mg_2NiH_4 , Figure 3c, with increased milling time. The presence of the intermetallic phase was confirmed by electron diffraction. The height and area of the Mg_2NiH_4 peak are equivalent to that of the primary Ni peak, implying a significant portion of the Ni catalyst has been transformed. The Ni peaks in the spectrum for the 1-hour milled specimen also exhibited a doublet peak located to the right of the main peak, which corresponds to a contraction of $\sim 1\%$. The area ratio for the fitted Ni (111) peak pair was ~ 2.5 (cf. Table 4). The Ni peaks for the 10-hour milled material, however, show no doublets.

The primary (200) MgO diffraction peak was present in both samples, Figure 3d, although it was of very low intensity in both cases. No differences in the size or shape of this oxide peak were seen between the 1- and 10-hour-milled spectra.

The mechanically milled mixtures of $\text{MgH}_2 + 0.05$ Ni consisted of aggregates – composed of MgH_2 and Ni particles – typically ranging in size from below 100 nm up to a few microns. Examples of the aggregate structures as a function of milling duration are compared in the SEM images presented in Figure 4. The wide range of agglomerate sizes was independent of the milling duration. The only noticeable effect was on the roughness of the aggregate surface, which appeared to increase with milling time; this roughness was not quantified.

The microstructure and the crystal structure of the aggregates are compared in the bright-field electron micrographs and the accompanying selected area diffraction patterns presented in Figure 5. The electron diffraction patterns indicate a polycrystalline structure with randomness increasing with ball-milling duration. The polycrystalline nature of the aggregates is consistent with the contrast variations seen in the electron micrographs. The contrast variations from region

to region are consistent with a decreasing grain size with increasing milling duration; the overlapping of the grains through the thickness of the aggregate prohibited determination of the grain size distribution.

Independent of the milling time, an oxide layer covered the surface of the MgH_2 aggregates. This is seen in the EDS maps and SAED pattern shown in Figures 6 and 7, respectively. The oxygen map of the slow scan (500 ms dwell time) in Figure 6 clearly shows the outer oxide surface layer on the aggregate. The Ni particles in the slow scan appear as shells due to the high count rate from those regions oversaturating the X-ray detector. A fast scan using a shorter dwell time (100 ms) confirmed that the Ni particles are solid. A bright-field electron micrograph of a particle, the corresponding diffraction pattern, and a dark-field micrograph formed using a portion of a diffraction ring are presented in Figure 7. The presence of MgO is shown in Figure 7b and the 220 dark-field image shows oxide nano-particles of 1.2-3 nm in size. The oxide layers were noticeably rougher in the 5- and 10-hour milled specimens.

Prior to ball-milling, the Ni nanopowder selected for the catalyst consisted of spherical Ni nanoparticles 10-80 nm in diameter with the occasional sphere with a diameter of 0.5-2 μm (Figure S1 in Supporting Information). The shape, size, and dispersion of the Ni catalyst were found to vary considerably as milling time increased, with the Ni dispersion becoming finer and more uniform with increased milling time. This is seen in the representative HAADF-STEM images presented in Figure 8 and the EDS data presented in Figure 9. In the 1-hour milled specimen, Figure 8a-c, Ni particles were observed to be round (spherical or ovoid) or elongated (plate-like or more irregular in shape) and mixed into the MgH_2 aggregate clusters. The Ni particles were typically tens of nanometers across – round particles as small as 3 nm and as large as 86 nm across were observed – with the more elongated particles having aspect ratios between 2 and 9 although ones with aspect ratios of 17 were observed. Chemical mapping using EDS, Figure 9a, revealed that the Ni was primarily localized into these discrete Ni nanoparticles. After 5 hours of milling, Figure 8d-f, fewer discrete Ni nanoparticles were seen and these were rounder, more regular, and smaller than in the 1-hour specimen. Aspect ratios typically below 4 were now common. The EDS maps show that, while localized Ni particles remained, a more diffuse background level of Ni across the MgH_2 aggregates had formed, Figure 9b. After 10 hours of milling, Figure 8g-i, the discrete Ni nanoparticles had greatly diminished in number and a stronger, more uniform delocalized background level of Ni was observed, Figure 9c. Of the

distinguishable Ni particles that remained, the largest were only 10-20 nm in diameter. Many MgH₂ particles were seen to be covered with very small particles, < 5nm in size, Figure 8h-i. Attempts to chemically map these particles at a higher resolution were unsuccessful due to the degree of beam damage. EDS point spectra taken at various locations in these aggregates revealed Ni/Mg ratios of $\sim 0.04 \pm 0.1$, sufficiently consistent with the initial stoichiometry to conclude that the expected amount of Ni, while less directly visible, was still present in the material. Except where noted, the point spectra were taken at locations not immediately on a distinguishable Ni particle. Focusing the EDS probe directly onto a Ni particle yielded a significantly higher Ni/Mg ratio (0.25) than the lower, more uniform levels detected elsewhere.

In order to obtain a more precise and complete understanding of the dispersion of the Ni catalyst and its relation to the MgH₂, electron tomography was performed on a 1-hour milled specimen. A tilt series of HAADF-STEM micrographs was acquired every 2° over the angular range +76° to -72°, Movie M1 in Supporting Information. A micrograph from the tilt series is compared with a snapshot of the resulting tomogram in Figure 10; a movie of the visualized tomogram is included as Movie M2 in Supporting Information. The tomogram shows that most of the Ni catalyst resides on or just below the surface of the MgH₂ particles, at depths roughly equal to or less than the size of the nanoparticle. The Ni nanoparticles found further inside the MgH₂ tended to be smaller and more irregular in shape, while larger more spherical or ovoid Ni particles tended to be only partially pressed into the MgH₂ surface or to occupy the interstices between MgH₂ particles. The embedded depth of the Ni nanoparticles was measured from orthogonal slices through the reconstruction; Figure 10c-e shows these slices for three example Ni particles: (c) a small, 35 nm round interior particle, (d) a large, 71 x 83 nm ovoid exterior/interstitial particle, and (e) a 113 x 186 x 21 nm plate-like interior/near-sub-surface particle. The holes and channels in the MgH₂ particles, visible as darker regions, are evidence of beam damage. Their formation did not alter the size, shape, or location of the Ni, and was completed before the acquisition of the tilt series.

3.3 Changes in Morphology and Catalyst Dispersion with Dehydrogenation

Specimens of all three milling durations were dehydrogenated via *in situ* S/TEM heating to 300 °C to investigate the evolution of the synthesized structures during hydrogen desorption. HAADF-STEM images showing the microstructure before and after desorption are presented in

Figure 11. For the 1 hr-milled material, desorption causes the formation of large hollows; examples are indicated by arrows in Figure 11d. On the exterior of most of the 1-hour aggregates, gaps formed between the oxide layer and the inner material. Evidence for these gaps is shown in Figure 11g, in which the oxide is seen detached from the aggregate. This is attributed to the underlying MgH_2 contracting during decomposition to the higher density Mg phase.

In contrast, most 5- and 10-hour specimens exhibited a smooth shell encasing agglomerated Mg particles on desorption. Examples are shown in Figure 11e and h and Figure 11f and i for the 5-hour and 10-hour-milled samples, respectively. This contraction of the Mg particles from the oxide layer had the added benefit of making the structure of the oxide easier to distinguish, confirming that it fully surrounded the Mg/ MgH_2 material. These changes and differences are not attributable to electron beam damage due to prior examination as they were also observed in non-tracked particles.

EDS chemical mapping of aggregates both before and after dehydrogenation, Figure 12, reveal changes in the Ni catalyst. For the 1-hour- and 5-hour-milled material, the distinct, localized Ni particles became less distinct; examples are indicated by arrows. In contrast, in the 10-hour-milled material, there appeared to be a slight reagglomeration of Ni.

In situ desorption experiments were also run in CTEM mode; Figure 13 shows the post-dehydrogenation images and diffraction patterns of the aggregates from Figure 5. The contrast mottling of the Mg particles in all three materials following dehydrogenation was on a larger scale and more uniform in overall contrast than the MgH_2 , implying a coarsening of grain size. The corresponding SAED patterns show a significant reduction in non-MgO diffraction spots resulting in more discontinuous rings. No Mg was seen to exit the oxide shell during desorption, which may play some role in why no appreciable sintering of the particles occurred. The relative number of Mg_2Ni diffraction spots did increase during desorption in all materials, suggesting that more of the Ni was transformed into the intermetallic compound during desorption. The oxide layer did not noticeably change in thickness during desorption in any of the materials, nor did the MgO rings in the diffraction patterns become any less continuous. Compared to the 1- and 10-hour milled samples, the 5-hour material exhibited less shrinkage of the interior Mg away from the oxide layer, with the oxide layer often following the topology of the underlying material as it changed morphology. While this morphology and behavior was observed occasionally in the other two materials, it was considerably more prevalent in the 5-hour case.

4. Discussion

The results show that the size, shape, and dispersion of catalyst are dependent on the milling duration, but that it is not a linear extrapolation or simple correlation. Additionally, the Ni particle morphology and dispersion changes with hydrogen desorption, which might suggest steady-state may be achieved with an increasing number of cycles. Ni was lost to the formation of an intermetallic phase both with increased milling time as well as during desorption. The hydride aggregates for the three milling times were encompassed by thin nanocrystalline MgO shells that remained intact during dehydrogenation and through which no Mg exited.

The tomographic reconstruction performed on the 1-hour milled material showed that the Ni catalyst is not limited to the surface of the hydride particles; some Ni is embedded entirely inside. The Ni particles that appeared to be the least affected by ball-milling – larger and spherical or ovoid – were found exterior to the hydride, e.g., in the interstices between particles, while the Ni particles found inside were distorted and smaller, suggesting that the ratio of interior to exterior Ni will increase with milling time. The information gained using electron tomography highlights the value of pairing conventional SEM and S/TEM characterization with tomography to remove the ambiguity in catalyst dispersion.

The continued evolution of the Ni catalyst dispersion during dehydrogenation observed in the EDS mapping – and seen in the S/TEM micrographs – indicates that the as-milled structure of MgH₂/Ni system is metastable. Localized Ni nanoparticles become more diffuse and Ni that is already highly dispersed may agglomerate. This suggests that regardless of the initial synthesized state of the material, there may be one state into which all the microstructures will eventually evolve given enough cycles. This implies that the ability to tune the uptake and release characteristics of MgH₂/Ni systems via mechanical milling parameters may be rather limited, and provides an explanation for the observations of poor cyclic stability in Ni-doped MgH₂ materials [8, 22].

An increase in the formation of the intermetallic Mg₂NiH₄ with milling time was confirmed by XRD, and the relative increase in strength and number of the Mg₂Ni spots in the electron diffraction patterns after desorption implies that the transformation of the Ni into Mg₂Ni may be a process that continues as the material is cycled. The latter observation is consistent with Hanada et al. [22], who noted the appearance of Mg₂Ni in the XRD spectrum of a

dehydrogenated specimen. This consumption of Ni to form the intermetallic during dehydrogenation also agrees with the decrease in distinctness of the discrete Ni particles during heating that was observed in the 1- and 5-hour specimens. The slight reagglomeration seen in some 10-hour specimens may be a coalescence of Mg_2Ni which had been highly dispersed during the ball-milling procedure.

As seen in the CTEM micrographs and the corresponding electron diffraction patterns, the outer oxide shells on the MgH_2 aggregates appear to be quite stable. MgO surface layers are normally considered to be nearly impermeable, or at least highly retarding, to hydrogen diffusion and a reason for diminished sorption performance [43-47]. In these specimens, however, desorption still occurred at much lower temperatures than bulk MgH_2 , especially in the 1-hour sample, and the oxide shells on these specimens were not observed to rupture during dehydrogenation. This indicates that either the MgO layers in these samples are sufficiently permeable to hydrogen to allow a reasonable rate of diffusion – perhaps due to the very small-grained polycrystalline nature of the oxide – or are sufficiently porous to allow access to the underlying MgH_2/Mg , or both. The ability of the material to function even in the presence of an oxide layer is important for practical application, where some degree of oxidation may prove unavoidable. The higher desorption temperatures observed in the 5- and 10-hour specimens may indicate that the oxide layer becomes more prevalent or less porous with increasing milling times. Although the oxide shells in the current study appeared to be structurally stable over the course of a single dehydrogenation, it is unknown how the shells will hold up to repeated cycling, and whether or not the stresses from the volumetric changes will eventually cause the shell to be broken apart. In the 1- and 10-hour milled material where, during dehydrogenation, the Mg appears to be surrounded in oxide shells that largely retained their size, the oxide shell, if it remains sufficiently intact, may help reduce sintering between the Mg particles during cycling, promoting greater cyclic stability. In a study of Mg thin-film model systems, Ostenfeld and Chorkendorff found that capping the film with an MgO layer, while it delayed hydrogen desorption, stabilized the underlying Mg, preventing otherwise significant amounts of Mg sublimation at temperatures around 177 °C that led to rapid sintering in equivalent oxide-free Mg films [46].

The tracking of individual particles before and after desorption allowed the evolved morphology to be directly compared with its initial state. It was observed that, as it

dehydrogenated, the MgH_2 shrank away from the outer oxide layer leaving behind oxide shells. These shells did not significantly change size or shape, being partially filled with Mg, which possesses a higher density than MgH_2 and thus occupies a lower volume. Empty oxide shells, which were occasionally observed, were the result of the Mg inside the shell being drawn away through a neighboring, attached aggregate. No Mg was found outside the oxide layer, nor was the oxide layer seen to have ruptured, allowing Mg to escape. This result is counter to the proposition of Montone et al. [48] that Mg is ejected during desorption, which was used to explain partially empty oxide shells. Nor was any concentration of catalyst inside the shell, segregated from the ejected Mg, observed in the current work. The ability to directly compare the evolved structures in the same particles enables determination of how these structures formed.

The desorption process exhibits changing behaviors associated with different desorption mechanisms, evidenced by the presence of various peaks in the TGA desorption data. For longer ball-milling times the desorption processes show distinct contributions from two or more different mechanisms while for the shortest milling time there is a continuous change initially converging to two distinct processes. The gradual onset of desorption in the 1-hr milled material is likely due to the inhomogeneity of MgH_2 crystallite size and Ni particle size and dispersion remaining after such a short milling duration. The sharpening of the onset seen with further milling is consistent with this interpretation, as a greater uniformity of size, shape, and distribution of MgH_2 crystallites and Ni with increased milling time was observed in S/TEM.

The trend in the onset temperatures of dehydrogenation may be explained by the "pathway effect" [49]. After only 1 hour of milling, most of the Ni particles reside on or partially embedded into the hydride surface where they could pierce the outer oxide and provide a pathway through it, resulting in the lower onset temperature. With additional milling, the Ni becomes more fully encapsulated in the MgH_2 and bound into intermetallics, both of which reduce the pathway effect, resulting in the increased onset temperatures of the 5- and 10-hr milled samples. At higher temperatures, dehydrogenation becomes more controlled by bulk diffusion, which is accelerated by reduced crystal size, explaining why the 10-hr milled material possessed the highest desorption rate. This indicates a trade-off between the two enhancements with milling duration. After 1 hour of milling, the pathway effect is strongest due to elemental Ni traversing the MgH_2 surface, and therefore the oxide, though diffusion through the bulk remains

rather slow. The 5 hour milling duration is long enough to lose most of the pathway effect, encapsulating or forming intermetallics with too much of the Ni, but too short to increase the bulk diffusion appreciably. 10 hours of milling, however, appears to be sufficient to increase bulk diffusion. This suggests that an initial milling duration of 10 hours without Ni followed by a short 1 hour milling with Ni might maximize both effects.

In the 1-hr milled specimen, the majority of the hydrogen release is associated with the process corresponding to the peak at 255 °C. As milling duration increases, however, a peak at 270 °C becomes increasingly dominant, accounting for almost the entire desorption after 10 hours of milling. Taken with the absence of the 270 °C peak in the 1-hr sample, this suggests the process associated with this peak is related to the increased formation of the intermetallic $\text{Mg}_2\text{Ni}/\text{Mg}_2\text{NiH}_4$ with increased milling times. The increased transformation of Ni into the intermetallic compound may also contribute to the higher desorption temperatures. While this intermetallic entity can function as a hydrogen storage material in its own right, albeit with significantly lower hydrogen capacity, it may not be as effective a catalyst as pure Ni. Binding the Ni in Mg_2Ni effectively decreases the amount of Ni available to serve as a catalyst. This is in agreement with Hanada et al., who found that the catalytic ability of Mg_2Ni was weaker than that of pure Ni metal [22]. Adding more Ni might initially mitigate these losses, but doing so also reduces the hydrogen storage capacity of the material. If the degradation in performance is indeed due to the formation of Mg/Ni intermetallic material, one potential solution is to select a catalyst, such as Ti, which exhibits a low affinity, unlike Ni, for forming compounds with Mg.

The prefactors associated with each desorption step imply that the primary impact of varying ball-milling duration is on the number and type of reaction site for desorption rather than on any particular activation energy. The prefactor for the 255 °C “surface catalyzed” reaction is the highest (90×10^{13}), possibly indicating many sites for reaction. For the 295 °C “bulk” reaction, the prefactor is much lower (5×10^{13}), indicating far fewer sites for reaction. The 270 °C reaction, attributed here to the heavily milled nanocrystalline bulk, shows an increased prefactor (35×10^{13}) rather than a changed E_a . It should be noted that the specific values of the activation energies and prefactors should be considered within the context of the experimental conditions.

The relative height of the desorption peak at 295 °C varied between the different samples, being highest in the 5-hr milled sample, but no clear trend could be distinguished with the limited data set available and would require further investigation. The same applies to the higher-

temperature peak around 330 °C that is only present in the 5-hr milled specimen. One possibility would be if the 5-hr specimen had been oxidized to a greater degree than the others, though it is uncertain whether this or a different process altogether is responsible for the additional complexity.

The origin of the doublets observed in the XRD spectra for the 1-hour-milled material is currently uncertain. The doublet spacing, listed in Table 3, is too wide to be accounted for by $\text{Cu K}_\alpha\text{-K}_\beta$ splitting. The spacing also increases with angle in a manner consistent with a physical change in the material rather than an instrumental effect. The Ni-doped specimens evolve gas between two and three hours into the scan, evidenced by a slight bowing out of the Kapton film, but this cannot be the reason for the doublets since they are present even in the earlier peaks. It is more likely that the doublets are due to a second phase, or phases, of material. Since all MgH_2 peaks exhibit a doublet, the second phase possesses the same tetragonal crystal structure as MgH_2 but a smaller lattice spacing. This could be explained by some amount of non-stoichiometric magnesium hydride. The presence of doublets on the Ni peaks in the 1-hour but not 10-hour Ni-doped specimens could be due to Mg-Ni alloying. While the two are immiscible in equilibrium, high-energy ball-milling can induce non-equilibrium changes as well as introduce a large number of vacancies into the system. Mg-Ni alloying in the 1-hour specimen could be the precursor to the formation of Mg_2NiH_4 intermetallic material with continued milling; the intermetallic compound was not formed immediately. This would explain the disappearance of the Ni doublets and the presence of the Mg_2NiH_4 peak in the 10-hour spectrum.

5. Conclusions

In this work, the effects of milling duration and hydrogen desorption on the morphologies and catalyst dispersions of high-energy ball-milled Ni-catalyzed MgH_2 were investigated. The Ni catalyst particles were highly localized after 1 hour of milling, but with increasing milling duration particle size decreased non-linearly and the discrete Ni particles produced a more uniform background of Ni after 10 hours. As milling time increased, more Ni was transformed into the intermetallic Mg_2NiH_4 , which provides an explanation for the increased desorption temperatures observed. This has implications for the selection of catalytic species, suggesting that hydride-catalyst pairs be chosen with low miscibility. Electron tomography revealed that

after 1 hour of milling, the Ni particles resided both outside and inside the MgH_2 , and suggested that the ratio of interior to exterior Ni increases with milling duration.

The as-synthesized catalyst morphology and dispersions were not stable with dehydrogenation. A redistribution of catalyst was observed as well as the continued loss of Ni to the formation of the intermetallic phase. This could explain the degradation in sorption kinetics reported in this system, and indicates there may be a steady-state structure achieved with increasing hydrogen cycling.

Nanocrystalline MgO shells enclosed the MgH_2 particle aggregates of all three milling durations studied. The oxide shells remained intact with desorption, with no egress of Mg observed. The oxide layers in the 5- and 10-hour material were noticeably rougher than in the 1-hour material, indicating that the details of this oxide layer may be an important factor in sorption.

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References

1. Züttel, A., Remhof, A., Borgschulte, A., and Friedrichs, O., *Hydrogen: the future energy carrier*. Philos Trans R Soc London Ser A, 2010. **368**(1923): p. 3329-3342.
2. Grochala, W. and Edwards, P.P., *Thermal Decomposition of the Non-Interstitial Hydrides for the Storage and Production of Hydrogen*. Chem Rev, 2004. **104**(3): p. 1283-1316.
3. Yang, J., Sudik, A., Wolverton, C., and Siegel, D.J., *High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery*. Chem Soc Rev, 2010. **39**(2): p. 656-675.
4. Sakintuna, B., Lamari-Darkrim, F., and Hirscher, M., *Metal hydride materials for solid hydrogen storage: A review*. Int J Hydrogen Energy, 2007. **32**(9): p. 1121-1140.
5. Orimo, S.-i., Nakamori, Y., Eliseo, J.R., Züttel, A., and Jensen, C.M., *Complex Hydrides for Hydrogen Storage*. Chem Rev, 2007. **107**(10): p. 4111-4132.
6. Stampfer, J.F., Holley, C.E., and Suttle, J.F., *The Magnesium Hydrogen System*. J Am Chem Soc, 1960. **82**(14): p. 3504-3508.

7. Vigeholm, B., Kjølner, J., Larsen, B., and Pedersen, A.S., *Formation and decomposition of magnesium hydride*. J Less-Common Met, 1983. **89**(1): p. 135-144.
8. Bogdanović, B., Hartwig, T.H., and Spliethoff, B., *The development, testing and optimization of energy storage materials based on the MgH_2 -Mg system*. Int J Hydrogen Energy, 1993. **18**(7): p. 575-589.
9. Bogdanović, B., Bohmhammel, K., Christ, B., Reiser, A., Schlichte, K., Vehlen, R., and Wolf, U., *Thermodynamic investigation of the magnesium-hydrogen system*. J Alloys Compd, 1999. **282**(1-2): p. 84-92.
10. Jain, I.P., Lal, C., and Jain, A., *Hydrogen storage in Mg: A most promising material*. Int J Hydrogen Energy, 2010. **35**(10): p. 5133-5144.
11. Aguey-Zinsou, K.-F. and Ares-Fernandez, J.-R., *Hydrogen in magnesium: new perspectives toward functional stores*. Energy Environ Sci, 2010. **3**(5): p. 526-543.
12. Zaluska, A., Zaluski, L., and Strom-Olsen, J.O., *Nanocrystalline magnesium for hydrogen storage*. J Alloys Compd, 1999. **288**(1-2): p. 217-225.
13. Varin, R.A., Czujko, T., Chiu, C., and Wronski, Z., *Particle size effects on the desorption properties of nanostructured magnesium dihydride (MgH_2) synthesized by controlled reactive mechanical milling (CRMM)*. J Alloys Compd, 2006. **424**(1-2): p. 356-364.
14. Aguey-Zinsou, K.F., Ares Fernandez, J.R., Klassen, T., and Bormann, R., *Using MgO to improve the (de)hydriding properties of magnesium*. Mater Res Bull, 2006. **41**(6): p. 1118-1126.
15. Huot, J., Liang, G., and Schulz, R., *Mechanically alloyed metal hydride systems*. Appl Phys A-Mater, 2001. **72**(2): p. 187-195.
16. Schulz, R., Huot, J., Liang, G., Boily, S., Lalande, G., Denis, M.C., and Dodelet, J.P., *Recent developments in the applications of nanocrystalline materials to hydrogen technologies*. Mater Sci Eng, A, 1999. **267**(2): p. 240-245.
17. Hanada, N., Ichikawa, T., Orimo, S.-I., and Fujii, H., *Correlation between hydrogen storage properties and structural characteristics in mechanically milled magnesium hydride MgH_2* . J Alloys Compd, 2004. **366**(1-2): p. 269-273.
18. Bérubé, V., Radtke, G., Dresselhaus, M., and Chen, G., *Size effects on the hydrogen storage properties of nanostructured metal hydrides: A review*. Int J Energy Res, 2007. **31**(6-7): p. 637-663.
19. Friedrichs, O., Aguey-Zinsou, F., Fernández, J.R.A., Sánchez-López, J.C., Justo, A., Klassen, T., Bormann, R., and Fernández, A., *MgH_2 with Nb_2O_5 as additive, for hydrogen storage: Chemical, structural and kinetic behavior with heating*. Acta Mater, 2006. **54**(1): p. 105-110.
20. Liang, G., Huot, J., Boily, S., Van Neste, A., and Schulz, R., *Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH_2 -Tm (Tm=Ti, V, Mn, Fe and Ni) systems*. J Alloys Compd, 1999. **292**(1-2): p. 247-252.
21. Shang, C.X., Bououdina, M., Song, Y., and Guo, Z.X., *Mechanical alloying and electronic simulations of (MgH_2 +M) systems (M=Al, Ti, Fe, Ni, Cu and Nb) for hydrogen storage*. Int J Hydrogen Energy, 2004. **29**(1): p. 73-80.
22. Hanada, N., Ichikawa, T., and Fujii, H., *Catalytic effect of nanoparticle 3d-transition metals on hydrogen storage properties in magnesium hydride MgH_2 prepared by mechanical milling*. J Phys Chem B, 2005. **109**(15): p. 7188-7194.

23. Oelerich, W., Klassen, T., and Bormann, R., *Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials*. J Alloys Compd, 2001. **315**(1–2): p. 237-242.
24. Song, M., Bobet, J.-L., and Darriet, B., *Improvement in hydrogen sorption properties of Mg by reactive mechanical grinding with Cr_2O_3 , Al_2O_3 and CeO_2* . J Alloys Compd, 2002. **340**(1–2): p. 256-262.
25. Guoxian, L., Erde, W., and Shoushi, F., *Hydrogen absorption and desorption characteristics of mechanically milled Mg-35wt.%FeTi_{1.2} powders*. J Alloys Compd, 1995. **223**(1): p. 111-114.
26. Terzieva, M., Khrussanova, M., and Peshev, P., *Hydriding and dehydriding characteristics of Mg-LaNi₅ composite materials prepared by mechanical alloying*. J Alloys Compd, 1998. **267**(1–2): p. 235-239.
27. Zhou, C., Fang, Z.Z., Ren, C., Li, J., and Lu, J., *Effect of Ti Intermetallic Catalysts on Hydrogen Storage Properties of Magnesium Hydride*. J Phys Chem C, 2013. **117**(25): p. 12973-12980.
28. Eisenberg, F.G., Zagnoli, D.A., and Sheridan Iii, J.J., *The effect of surface nickel on the hydriding-dehydriding kinetics of MgH₂*. J Less-Common Met, 1980. **74**(2): p. 323-331.
29. Friedlmeier, G. and Groll, M., *Experimental analysis and modelling of the hydriding kinetics of Ni-doped and pure Mg*. J Alloys Compd, 1997. **253–254**(0): p. 550-555.
30. Pelletier, J.F., Huot, J., Sutton, M., Schulz, R., Sandy, A.R., Lurio, L.B., and Mochrie, S.G.J., *Hydrogen desorption mechanism in MgH₂-Nb nanocomposites*. Phys Rev B, 2001. **63**(5): p. 052103.
31. Bazzanella, N., Checchetto, R., and Miotello, A., *Catalytic effect on hydrogen desorption in Nb-doped microcrystalline MgH₂*. Appl Phys Lett, 2004. **85**(22): p. 5212-5214.
32. Larsson, P., Araújo, C.M., Larsson, J.A., Jena, P., and Ahuja, R., *Role of catalysts in dehydrogenation of MgH₂ nanoclusters*. Proc Nat Acad Sci, 2008. **105**(24): p. 8227-8231.
33. Jensen, T.R., Andreasen, A., Vegge, T., Andreasen, J.W., Ståhl, K., Pedersen, A.S., Nielsen, M.M., Molenbroek, A.M., and Flemming, B., *Dehydrogenation kinetics of pure and nickel-doped magnesium hydride investigated by in situ time-resolved powder X-ray diffraction*. Int J Hydrogen Energy, 2006. **31**(14): p. 2052-2062.
34. Aguey-Zinsou, K.F., Ares Fernandez, J.R., Klassen, T., and Bormann, R., *Effect of Nb₂O₅ on MgH₂ properties during mechanical milling*. Int J Hydrogen Energy, 2007. **32**(13): p. 2400-2407.
35. Choi, Y.J., Lu, J., Sohn, H.Y., Fang, Z.Z., and Rönnebro, E., *Effect of Milling Parameters on the Dehydrogenation Properties of the Mg–Ti–H System*. J Phys Chem C, 2009. **113**(44): p. 19344-19350.
36. Lu, J., Choi, Y.J., Fang, Z.Z., Sohn, H.Y., and Rönnebro, E., *Hydrogen Storage Properties of Nanosized MgH₂–0.1TiH₂ Prepared by Ultrahigh-Energy–High-Pressure Milling*. J Am Chem Soc, 2009. **131**(43): p. 15843-15852.
37. Polanski, M., Bystrzycki, J., Varin, R.A., Plocinski, T., and Pisarek, M., *The effect of chromium (III) oxide (Cr_2O_3) nanopowder on the microstructure and cyclic hydrogen storage behavior of magnesium hydride (MgH₂)*. J Alloys Compd, 2011. **509**(5): p. 2386-2391.
38. Danaie, M. and Mitlin, D., *TEM analysis of the microstructure in TiF₃-catalyzed and pure MgH₂ during the hydrogen storage cycling*. Acta Mater, 2012. **60**(19): p. 6441-6456.

39. Tan, X., Zahiri, B., Holt, C.M.B., Kubis, A., and Mitlin, D., *A TEM based study of the microstructure during room temperature and low temperature hydrogen storage cycling in MgH₂ promoted by Nb–V*. *Acta Mater*, 2012. **60**(16): p. 5646-5661.
40. *EM3D: Software for Electron Microscope Tomography* (<http://em3d.stanford.edu/index.html>).
41. Pettersen, E.F., Goddard, T.D., Huang, C.C., Couch, G.S., Greenblatt, D.M., Meng, E.C., and Ferrin, T.E., *UCSF Chimera—A visualization system for exploratory research and analysis*. *J Comput Chem*, 2004. **25**(13): p. 1605-1612.
42. Schneider, C.A., Rasband, W.S., and Eliceiri, K.W., *NIH Image to ImageJ: 25 years of image analysis*. *Nat Meth*, 2012. **9**(7): p. 671-675.
43. Dehouche, Z., Goyette, J., Bose, T.K., and Schulz, R., *Moisture effect on hydrogen storage properties of nanostructured MgH₂–V–Ti composite*. *Int J Hydrogen Energy*, 2003. **28**(9): p. 983-988.
44. Hjort, P., Krozer, A., and Kasemo, B., *Hydrogen sorption kinetics in partly oxidized Mg films*. *J Alloys Compd*, 1996. **237**(1–2): p. 74-80.
45. Friedrichs, O., Sánchez-López, J.C., López-Cartes, C., Dornheim, M., Klassen, T., Bormann, R., and Fernández, A., *Chemical and microstructural study of the oxygen passivation behaviour of nanocrystalline Mg and MgH₂*. *Appl Surf Sci*, 2006. **252**(6): p. 2334-2345.
46. Ostenfeld, C.W. and Chorkendorff, I., *Effect of oxygen on the hydrogenation properties of magnesium films*. *Surf Sci*, 2006. **600**(6): p. 1363-1368.
47. Ostenfeld, C.W., Johansson, M., and Chorkendorff, I., *Hydrogenation properties of catalyzed and non-catalyzed magnesium films*. *Surf Sci*, 2007. **601**(8): p. 1862-1869.
48. Montone, A., Aurora, A., Gattia, D.M., and Antisari, M.V., *Microstructural and Kinetic Evolution of Fe Doped MgH₂ during H₂ Cycling*. *Catalysts*, 2012. **2**(3): p. 400-411.
49. Friedrichs, O., Sánchez-López, J.C., López-Cartes, C., Klassen, T., Bormann, R., and Fernández, A., *Nb₂O₅ “Pathway Effect” on Hydrogen Sorption in Mg*. *J Phys Chem B*, 2006. **110**(15): p. 7845-7850.

Table 1. Dehydrogenation values extracted from TGA heating experiments. The values listed in parentheses are from a second set of samples.

Table 2. Peak positions and fitting parameters for the curves fitted to the derivative weight loss TGA measurements. “n/a” means that component is not present in the desorption curves for that material. *The prefactors are about a factor of ten smaller for $E_a = 1.7$ eV, and a factor of ten larger for 1.9 eV.

Table 3. Locations and distances of the main and doublet peaks, measured from the fitted peaks in Figure 3, and the percent contraction of the matching lattice plane to which the peak corresponds.

Table 4. Areas and heights of the main and doublet peaks, measured from the fitted peaks in Figure 3, along with the total area and area ratio of the MgH₂ main/doublet peaks.

Figure 1. TGA (a) weight loss curves and (b) derivative weight loss curves for 1-, 5-, and 10-hour milled Ni-doped MgH_2 . These curves are from the first run. The onset temperatures and total weight losses determined from (a) are listed in Table 1.

Figure 2. Indexed powder XRD spectra for the 1- and 10-hour milled Ni-doped material and of the empty holder covered by the Kapton tape. The spectra have been offset in intensity for ease of comparison.

Figure 3. Selected enlarged peaks from the XRD spectra of the 1- and 10-hour milled material from Figure 2 (gray and black, respectively). Peak identities are labeled by each feature. Doublets are observed in the MgH_2 (a,c) and Ni (b) peaks of the 1-hour specimen. The primary Mg_2NiH_4 peak (c) is present in the 10-hour milled spectra. The MgO peak (d) is present and equivalent in both spectra.

Figure 4. SEM micrographs of MgH_2 aggregates from the (a) 1-, (b) 5-, and (c) 10-hour milled Ni-doped material in the as-milled state. All images are the same magnification.

Figure 5. TEM micrographs and accompanying electron diffraction patterns from example aggregates of (a) 1-, (b) 5-, and (c) 10-hour-milled material prior to *in situ* TEM heating to 300 °C. All scale bars are 50 nm.

Figure 6. EDS chemical mapping of a 1-hour milled Ni-doped MgH_2 aggregate. The slow scan (500 ms dwell time) clearly shows the outer oxide surface layer on the aggregate. The Ni particles appear as shells due to the high count rate from those regions oversaturating the X-ray detector. A fast scan using a shorter dwell time (100 ms) confirmed that the Ni particles are solid. The maps are 630 nm across and were acquired at Argonne National Laboratory.

Figure 7. (a) bright-field TEM micrograph of 1-hour milled Ni-doped MgH_2 with the corresponding MgO-indexed diffraction pattern. (b) dark-field TEM image formed with the objective aperture placed over a portion of the MgO (220) diffraction ring. The position of the aperture is shown by white circle on the diffraction pattern.

Figure 8. HAADF-STEM micrographs of 1- (a-c), 5- (d-f), and 10-hour (g-i) milled Ni-doped MgH_2 specimens in the as-synthesized state.

Figure 9. EDS chemical maps of 1-, 5-, and 10-hour milled specimens in the as-synthesized state. The dark-field intensity, Mg, and Ni maps are shown. All maps are 2.189 μm wide.

Figure 10. (a) HAADF-STEM micrograph from the tilt series of a 1-hour milled aggregate. (b) Tomographic reconstruction of the aggregate in (a) in a similar orientation. The Mg is colored blue and the Ni is colored yellow. (c-e) Orthographic slices through the reconstruction, showing the 3D relationship of three example Ni particles, indicated in (b), to the MgH_2 .

Figure 11. HAADF-STEM micrographs of 1-, 5-, and 10-hour milled specimens before (a-c) and after (d-i) *in situ* STEM heating to 300 °C. (a-f) are before/after image pairs of the same particles, while (g-i) are additional post-heat images to show detail. In (d), examples of the large

voids that formed during heating are outlined with dotted black lines and are indicated by arrows. The insets of (g) show higher magnification views of where the inner MgH_2 separated from the outer oxide layer. The outer oxide layer is indicated by white dotted lines, while the underlying Mg surface is indicated by solid white lines. All scale bars are 200 nm.

Figure 12. EDS chemical maps of 1-, 5-, and 10-hour milled specimens showing the same particle before and after *in situ* STEM heating to 300 °C. Arrows in the 1-hr and 5-hr images indicate examples of discrete Ni particles becoming more diffuse upon hydrogen desorption. The arrow in the 10-hr image indicates an example of potential Ni agglomerate with hydrogen desorption. All maps are 1.751 μm wide.

Figure 13. TEM micrographs and accompanying electron diffraction patterns from the same aggregates of (a) 1-, (b) 5-, and (c) 10-hour-milled material shown in Figure 3 but after *in situ* TEM heating to 300 °C. All scale bars are 50 nm.

Figure 01

Figure 02

Figure 03

Figure 04

Figure 05

Figure 06

Figure 07

Figure 08

Figure 09

Figure 10

Figure 11

Figure 12

Figure 13

Table captions listed at end of manuscript with the figure captions.

Table 1:

Milling Duration	Onset Temp (°C)	Total Weight % loss
1-hour	222 (215) $\pm$ 1	5.90 (5.92) $\pm$ 0.04
5-hour	244 (243) $\pm$ 1	5.72 (5.54) $\pm$ 0.04
10-hour	246 (249) $\pm$ 1	6.01 (5.88) $\pm$ 0.04

Table 2:

Peak Position (°C)	Ea (eV)	Prefactor*	1-hr milled Height (wt%)	5-hr milled Height (wt%)	10-hr milled Height (wt%)
255 $\pm$ 5	1.8 $\pm$ 0.1	9.0 $\times 10^{14}$	4.4 $\pm$ 0.2	0.35 $\pm$ 0.1	n/a
270 $\pm$ 5	1.8 $\pm$ 0.1	3.5 $\times 10^{14}$	n/a	2.3 $\pm$ 0.2	6.3 $\pm$ 0.3
295 $\pm$ 5	1.8 $\pm$ 0.1	5.0 $\times 10^{13}$	1.0 $\pm$ 0.1	2.7 $\pm$ 0.1	0.6 $\pm$ 0.1

Table 3:

Material	hkl	2θ Main (°)	2θ Doublet (°)	Separation (°)	Separation (nm)	Contraction (%)
MgH₂	110	27.65 $\pm$ 0.01	27.96 $\pm$ 0.01	0.30 $\pm$ 0.01	0.034 $\pm$ 0.002	1.06 $\pm$ 0.05
	101	35.50 $\pm$ 0.01	35.87 $\pm$ 0.01	0.37 $\pm$ 0.01	0.025 $\pm$ 0.001	1.00 $\pm$ 0.03
	200	39.68 $\pm$ 0.01	40.12 $\pm$ 0.01	0.44 $\pm$ 0.01	0.024 $\pm$ 0.001	1.04 $\pm$ 0.02
	211	54.41 $\pm$ 0.01	54.92 $\pm$ 0.01	0.51 $\pm$ 0.01	0.015 $\pm$ 0.001	0.86 $\pm$ 0.02
Ni	111	44.29 $\pm$ 0.01	44.73 $\pm$ 0.01	0.44 $\pm$ 0.01	0.019 $\pm$ 0.001	0.93 $\pm$ 0.01

Table 4:

Material	hkl	Area		Height		
		Main	Doublet	Main	Doublet	M/D
MgH ₂	110	80 ±11	71 ±6	215 ±20	204 ±14	1.05 ±0.12
	101	153 ±9	117 ±9	278 ±12	198 ±12	1.40 ±0.10
	200	66 ±4	44 ±3	131 ±7	118 ±8	1.11 ±0.09
	211	169 ±4	75 ±5	291 ±6	122 ±6	2.39 ±0.13
Ni	111	123 ±3	49 ±3	254 ±6	110 ±6	2.31 ±0.14
Total Area		468 ±15	307 ±12			
Area Ratio		1.52 ±0.08				