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Hydrogen Sorption Cycling Kinetic Stability and Microstructure of Single-Walled Carbon Nanotube (SWCNT) Magnesium Hydride (MgH₂) Nanocomposites

Babak Shalchi Amirkhiz,[†] Mohsen Danaie,[†] Michael Barnes,[‡] Benoît Simard,[‡] and David Mitlin^{*,†}

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada, National Institute for Nanotechnology, NRC, Edmonton, Alberta, Canada, and Steacie Institute for Molecular Sciences (SIMS), NRC, 100 Sussex Drive, Ottawa, Ontario, Canada

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We have examined comilling with unpurified single-walled carbon nanotubes (SWCNTs) as a method to promote hydrogenation/dehydrogenation cycling kinetic stability in nanocrystalline magnesium hydride (MgH₂). The synthesized material was a true nanocomposite consisting of MgH₂ covered by highly defective SWCNTs coupled to catalytic metal nanoparticles and mixed with amorphous carbon. The nanocomposite was hydrogen sorption cycled at 300 °C using a volumetric Sievert's type apparatus. Identically milled pure MgH₂ was used as a baseline. The microstructure of both materials was analyzed in detail using cryo-stage transmission electron microscopy (TEM) as well as other techniques. The nanocomposite shows markedly improved kinetic performance, both during initial postmilling desorption and during subsequent cycling. Activation energy analysis demonstrates that any catalytic effect due to the metallic nanoparticles is lost during cycling. Improved cycling performance is instead achieved as a result of the carbon allotropes preventing MgH₂ particle agglomeration and sintering. Even after 35 absorption/desorption cycles, the SWCNTs remain covering the MgH₂ surfaces. Sorption cycling creates a dramatic difference in the particle size distributions between the nanocomposite system and the baseline, whereas the two were nearly identical at the onset of testing. In a separate experiment performed at more aggressive pressure conditions, the nanocomposite received over 100 sorption cycles with fairly minor kinetic degradation.

Introduction

Composite metal–carbon nanostructures are a subject of increasing scientific inquiry due to their realized and potential hydrogen storage properties. A “traditional” use of carbon–metal nanostructures is for enhanced cryogenic hydrogen physisorption, e.g., refs 1–7. However, a recent approach that has achieved notable experimental success is the use of such nanostructures to enhance the kinetics of elevated temperature hydrogen chemisorption in metal and chemical hydrides. Early work on the addition of graphite to promote hydrogenation of magnesium was performed by Imamura and co-workers.^{8,9} Shortly afterward, Bouaricha et al. used a variety of carbon structures to enhance hydriding in Mg₂Ni, Mg, Ti, and V metals and FeTi intermetallics.^{10,11} Subsequent studies purposely combined metallic nanocatalysts with graphite to obtain a synergistic catalytic effect.^{12,13} Of the various carbon structures and allotropes, two approaches have been shown to be the most successful in enhancing the sorption kinetics. The first approach is the utilization of nanoporous/nanoscaffolded carbon structures for size confinement of the hydride phases, e.g., refs 14–17. The second methodology, which is the subject of this study, involves using carbon nanotubes (CNTs), usually combined with metallic nanoparticles, to enhance the sorption kinetics.^{18–28} In all cases, a kinetic sorption enhancement was reported following the comilling of the powders. For magnesium hydride, the summary below covers the pertinent literature.

Wu et al.¹⁸ examined the effects of using purified versus metal-containing (as-prepared) CNTs on the absorption/desorption properties of mechanically milled magnesium hydride. The authors found that the hydrogen desorption temperature was reduced by as much as 70 °C with the incorporation of the as-prepared CNTs into the system. The purified nanotubes were not as effective, lowering the endothermic peak temperature by 40 °C relative to the baseline. Using the kinetic Kissinger analysis, the authors reported that the activation energy for desorption was lowered from 126 kJ/mol for the baseline MgH₂ powder to 96 kJ/mol for the composite containing the metallic particles and CNTs. The activation energy for the hydride powder containing only the purified nanotubes was effectively the same as that of the baseline.

Yao et al.¹⁹ examined the cocatalytic effect of metal (FeTi) nanoparticles and CNTs on the sorption properties of magnesium hydride, using both experiments and density functional theory (DFT). The authors reported a clear synergistic effect on the kinetics of using both catalytic additions versus either one separately. In addition to the physical contributions that the CNTs had in facilitating mechanical milling, the authors proposed a chemical catalytic role as well. The hypothesized mechanism was essentially that the metallic nanoparticles enhance hydrogen dissociation (reassociation), whereas the nanotubes provide fast diffusion surfaces/channels for the hydrogen atoms to enter (exit) the magnesium (magnesium hydride). At temperatures above 300 °C, the carbon was also predicted to be somewhat catalytic toward hydrogen dissociation. In a subsequent manuscript, the same group of authors showed a similar, though even more enhanced, synergistic effect when V–Ti nanoparticles were combined with the CNTs.²⁰

* To whom correspondence should be addressed. E-mail: dmitlin@ualberta.ca.

[†] University of Alberta and National Institute for Nanotechnology, NRC.

[‡] Steacie Institute for Molecular Sciences (SIMS), NRC.

Lillo-Rodenas and co-workers investigated the addition of a variety of carbon allotropes mixed with Ni or Fe nanoparticles to magnesium hydride.²¹ The authors also examined the effect of limited absorption/desorption cycling (up to five cycles) on the microstructure and the sorption behavior. They reported enhanced desorption kinetics particularly in the carbon nanofiber containing samples. The multiwalled carbon nanotube (MWCNT) composites had the peak temperature of decomposition decrease by approximately 20 °C relative to the baseline hydride powder, while the composites with the nanofibers had a temperature reduction of 40 °C. The authors conclusively showed that there was no relationship between the surface area of the carbon materials and the decomposition temperature, since the very high surface area of activated carbon was only marginally effective in changing the desorption characteristics. Another key point that the authors demonstrated was that for a given carbon material (nanofibers) the metal loading tremendously influences their efficacy. Since the total metal nanoparticle loading was less than 0.4 wt %, which by itself would not have been enough to achieve a substantial kinetic enhancement, a catalytic synergy was confirmed.

Recent work on the microstructure–sorption properties relations in the CNT–magnesium hydride system was performed by Mitlin et al.²² For microstructural analysis, the authors utilized cryogenically cooled sample stage transmission electron microscopy (TEM). This kept the samples at 90 K and allowed for direct analysis of the hydride while incurring minimal electron-beam-induced artifacts. The researchers found that single-walled carbon nanotube (SWCNT)–metallic nanoparticle additions catalyze the desorption of hydrogen, lowering the activation energy by as much as 25 kJ/mol over those of identically milled pure MgH₂ powders. These optimum desorption properties were achieved after 1 h of high-energy comilling of the hydride and the SWCNTs. At longer milling times, the SWCNTs were completely destroyed and the enhancement was largely lost despite the continued presence of the metallic particles of the same scale as in the as-received materials.

While kinetic improvements in the initial desorption (absorption) behavior are promising results, a viable catalytic system must function through numerous hydrogen absorption/desorption cycles. In the case of the SWCNT (+ amorphous carbon) metal hydride system, this issue has received only limited attention. It is thus the goal of the current work. In parallel to characterizing the hydrogen sorption kinetics of SWCNT–magnesium hydride nanocomposites through numerous hydrogenation/dehydrogenation cycles, we aim to elucidate the fundamental surface and bulk microstructural features responsible for the observed trends. By acquiring an in-depth understanding of the structure in these nanomaterials, it will be possible to design and synthesize improved formulations.

Experimental Procedure

Magnesium hydride (MgH₂) powder was purchased from Gelest Inc. with 97 wt % purity, the balance being magnesium. Single-walled carbon nanotubes (SWCNTs) were fabricated using the laser ablation method²⁹ and were utilized in their as-processed state. The batches were actually a mixture of approximately 60 wt % amorphous carbon, 30 wt % SWCNTs with various wall widths, and 10 wt % of metallic (alloys containing various combinations of Co, Ni, Fe, and Y) nanoparticles used for growing the SWCNTs. In-house thermogravimetric analysis (TGA) under air was used to confirm these weight ratios. We combined the hydride powders with 5 wt % of the mixture (amorphous carbon, SWCNTs, transition metal

nanoparticles,). For the sake of brevity, we will refer to this exact mixture as SWCNT–MgH₂ nanocomposites with the understanding that the hydride is also covered with amorphous carbon and with metal particles.

The mixture was milled for different durations in a Fritsch Pulverisette 6 planetary monomill. We used a 10:1 ball to powder weight ratio, with agate balls and vial at 650 rpm rotation speed. Milling and all sample handling were performed inside a high-purity argon filled glovebox with the amount of oxygen and water vapor present being less than 0.1 ppm. The SWCNTs were comilled with the MgH₂ powder for various durations, though only the 1 h comilled samples (optimum properties) were used for sorption cycling. For the baseline analysis, the as-received MgH₂ powder was milled for 1 h.

Volumetric absorption and desorption measurements were performed using a Sievert's hydrogen sorption analysis system (Hy-Energy LLC, PCTPro 2000). All of the measurements were carried out at 300 °C. Two types of pressures were employed. The MgH₂ and SWCNT–MgH₂ powders that were analyzed for 10 and 35 cycles, respectively, were absorbed at a starting pressure of 10 bar (finishing at 7 bar) and desorbed at a starting pressure near 0.1 bar (finishing at 0.4 bar). These are also the specimens that received all of the subsequent microstructural characterization. As a follow up to the initial work, we performed extended cycling on the SWCNT–MgH₂ system. Hydrogen was absorbed at a starting pressure of 11 bar (finishing at 4 bar) and desorbed at a starting pressure of 0.04 bar (finishing at 0.2 bar). No additional microstructural characterization was performed on these specimens.

In addition, we also used a simultaneous differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) (SDT Q600, TA Instruments) to ascertain the hydrogen desorption kinetics. The analysis was performed under a constant flow of high-purity (99.998% pure) argon to prevent oxidation. Kissinger analysis³⁰ was employed to measure the activation energy of desorption. The method developed by Kissinger allows for obtaining the activation energy for a chemical reaction of any order by considering the variation of the temperature at the maximum reaction rate. In the case of endothermic hydride to metal transformation, the maximum reaction rate is straightforward to obtain from the constant heating rate DSC data and corresponds to the minimum of the desorption DSC peak. The Kissinger analysis can be expressed in the following form: $d(\ln(\varphi/T_m^2))/d(1/T_m) + E/R = \text{const}$, where φ is the heating rate, T_m is the absolute temperature at the maximum reaction rate, E is the activation energy, and R is the gas constant. The activation energy is obtained from a linear plot of $\ln(\varphi/T_m^2)$ versus $1/T_m$. For this analysis, the heating rates used were 10, 20, 25, and 30 °C/min.

The effect of comilling SWCNTs on the hydrogen desorption thermodynamics of MgH₂ was investigated using a high-pressure differential scanning calorimetry technique (HP-DSC).³¹ The technique relies on heating the samples at various pressures at a sufficiently slow rate that the onset of desorption occurs at an equilibrium temperature as dictated by the van't Hoff equation: $\ln p = \Delta H^0/RT - \Delta S^0/R$, where p is the pressure and p_0 is 1 atm, ΔH^0 is the enthalpy of hydride formation for MgH₂, and ΔS^0 is -130 J/mol K. Since desorption in MgH₂ is a single chemical reaction process with no intermediate states, by monitoring the onset of desorption (endothermic) for at least three hydrogen pressures, it is possible to obtain relatively accurate values of ΔH^0 . We used a TA Instruments Q20P dedicated pressure DSC system and performed the test at 0.5 °C/min.

Figure 1. (A) BET specific surface area versus milling time, for both the SWCNT–MgH₂ system and the MgH₂ baseline. Optimum dispersion of the SWCNTs on the MgH₂ surfaces is achieved after 1 h of comilling, as evidenced by a sharp peak in the BET surface area. (B) A TEM micrograph that illustrates the dispersion on the SWCNTs on the MgH₂ metal surfaces. The arrows in the figure point to the regions where the MgH₂ is in contact with the SWCNTs.

To analyze the released gas and confirm negligible hydrocarbon evolution during dehydrogenation, we combined mass spectroscopy with a thermal gravimetric analyzer and studied the gas evolution. The samples were analyzed on a Netzsch TG/MS/FTIR system (Netzsch TG 209 F1 Iris coupled to an Aëolos QMS403C mass spectrometer and a Bruker Tensor 27 Fourier Transform Infrared spectrometer via a TGA A588 TGA-IR module) under a flow of ultrahigh pure argon (99.9993%) to avoid oxidation during the runs. The powders were analyzed in an aluminum oxide crucible, and any residual oxygen atmosphere was removed by repeated chamber evacuation and argon gas refill. Powders were heated from ambient temperature to 550 °C at a heating rate of 10 °C/min, with a 20 min hold at 120 °C and a 30 min bake at 550 °C. The mass spectroscopy of evolved gases was measured from a mass range of 1–50 mass units.

To analyze the surface area of the composites and compare them to that of as-milled MgH₂ samples, a Quantachrome Autosorb 1 MP automatic gas adsorption system was used. The system is dedicated to standard measurements of nanostructured materials by nitrogen sorption isotherms at 77 K. Multipoint BET surface area measurement was done using ASiWin, version 1.5, software which supports the BET data reduction algorithm. All of the samples were degassed at 150 °C under a vacuum for at least 5 h prior to the tests.

X-ray diffraction (XRD) was utilized for grain size and microstrain determination in the as-milled and cycled samples. A Bruker-AXS, D8 Discover diffractometer system with an area detector and Cu K α radiation was used for the XRD experiments. XRD spectra were also analyzed for grain and lattice strain measurement. Integral breadth analysis (IBA) was utilized for deconvoluting the broadening effects of grain size and lattice strain for the powders. The following relation was used:³² $(\delta 2\theta)^2 / \tan^2 \theta_0 = K\lambda / D(\delta 2\theta / \tan \theta_0 \sin \theta_0) + 16e^2$, and $(\delta 2\theta)^2 / \tan^2 \theta_0$ was plotted versus $(\delta 2\theta / \tan \theta_0 \sin \theta_0)$, where $\delta 2\theta$ is the integral breadth of the peaks and θ_0 is the position of the peak maximum. K is a constant taken as 0.9, and λ is the X-ray wavelength (1.54 Å). The grain size (D) and microstrain (root mean squared strain) (e) can be calculated from the fitted line slope and ordinate intercept, respectively. The microstrain peak broadening is normally ascribed to the presence of nonuniform lattice strain due to dislocations. However, twins are also known to contribute to the broadening as well.³³ We used the first three α -MgH₂ peaks for the analysis. Instrumentation broadening was automatically accounted for in the analysis.

TEM analysis was performed using the JEOL 2010 and JEOL 2200FS microscopes, both operating at 200 kV accelerating voltage. Conventional bright field and dark field TEM analysis of α -MgH₂ was performed using a cryogenic holder held near 90 K. This was done to significantly increase the stability time of the hydride powder under the electron beam.³⁴ At cryogenic temperature, sample degradation occurred relatively slowly. Even in the milled sample, only slight weakening of the hydride reflections occurred after several minutes of beam exposure of one area. This was long enough to do the analysis. TEM samples were prepared by dry dispersing the powders onto amorphous carbon grids. We used the commercial software Desktop Microscopist for simulating experimental electron diffraction (SAD) patterns. Previously reported crystallographic data were used for generating the simulations of α -MgH₂ and Mg.³⁵ In the simulations, hydrogen superlattice reflections were excluded, since their intensity is significantly less than that of the magnesium atoms. We utilized Raman spectroscopy to track the structural changes of the SWCNTs versus cycling. Raman spectra of the MgH₂–SWCNT composites were obtained with a HORIBA iHR550 using 770.5 nm at 8 W, collected in the backscattering geometry at room temperature.

Results

Figures 1–3 provide information on the microstructure and the desorption behavior of the SWCNT–MgH₂ system and of the baseline MgH₂, both systems in the as-milled condition. While the remainder of the manuscript concerns the cycling behavior, these three figures are included to provide the proper background for the subsequent analysis. The as-received SWCNTs are in bundles that are deagglomerated during high-energy mechanical milling.²² Figure 1A shows a plot of the BET specific surface area versus milling time, for both the SWCNT–MgH₂ system and for the MgH₂ baseline. Optimum dispersion of the SWCNTs on the MgH₂ surfaces is achieved at 1 h of comilling, as evidenced by a sharp peak in the BET surface area. Comilling for 1 h also damages the SWCNTs, as evidenced by their Raman spectra.²² The 1 h comilled process condition was the one used for the cycling experiments. At 7 h of comilling, the SWCNTs are destroyed and the BET surface area decreases to the baseline level.

Figure 1B shows a TEM micrograph that illustrates the dispersion of the SWCNTs on the MgH₂ particle surfaces. The arrows in the micrograph point to the SWCNTs that are discernible in a two-dimensional projection of the TEM image.

Figure 2. TGA 1 h milled SWCNT–MgH₂ with mass 2 overlay and first order derivative of TG (DTG).

Figure 3. Van't Hoff plots for enthalpy of desorption comparing baseline MgH₂ and SWCNT–MgH₂ nanocomposites. The data was obtained from constant heating rate, variable pressure HP-DSC analysis.

A metal nanoparticle attached to a nanotube (second arrow from the left) is also visible on the hydride surface. The SWCNTs along with the amorphous carbon and the metallic nanoparticles completely cover the hydride powder, creating a nanocomposite microstructure. As will be shown in the subsequent text and figures, the SWCNTs survive multiple hydrogenation/dehydrogenation cycles.

Figure 2 shows the gas evolution results of the SWCNT–MgH₂ nanocomposites after 1 h of milling. The sample was heated to 120 °C at a rate of 10 °C/min, held at 120 °C for 20 min, heated to 550 °C at a rate of 10 °C/min, and then held at 550 °C for 30 min. Gas evolution was monitored by mass spectroscopy (MS). This experiment was repeated twice with nearly identical results. The peak rate of hydrogen desorption occurred at 360 °C. No hydrocarbon emission was detected at temperatures where hydrogen was evolved. The hydrogen loss in the composites was measured to be 5.7 wt %. Figure 3 shows the HP-DSC results for both systems. As expected, comilling MgH₂ with SWCNTs does not alter the enthalpy of magnesium hydride desorption. Thus, we can state from the onset that the beneficial effects of the SWCNTs, which will be demonstrated in the subsequent figures, are related to kinetics and not to any changes in the system thermodynamics.

Figure 4 shows representative absorption and desorption cycling data for the baseline milled MgH₂ powder (A and B) and for the SWCNT-covered MgH₂ (C and D). The hydrogen sorption kinetics of both systems do degrade after prolonged cycling. However, the rate and the magnitude of the degradation are very different between the nanocomposite and the baseline. The baseline powder was desorption/absorption cycled 10 times. The nanocomposite powder was cycled up to 35 cycles using the same pressure conditions as the baseline. By cycle 10, the MgH₂ baseline is able to absorb (desorb) less than 4 wt % (3 wt %) hydrogen in 0.6 (2.5) h. Conversely, the nanocomposite powder still sorbs approximately 5 wt % in the same time increments.

Figure 5 compares the times to absorb (desorb) 4 wt % hydrogen for the SWCNT–MgH₂ nanocomposite versus the baseline MgH₂. The nanocomposite was tested at two sets of pressure conditions. The samples that were tested for 35 cycles received the same sorption regiment as the baseline powder: 10 bar absorption and 0.1 bar desorption. These were the specimens whose microstructure was analyzed in detail. Later, a second set of experiments was performed where the nanocomposite was cycled using more aggressive pressures: 11 bar absorption and 0.04 bar desorption. These samples were tested

Figure 4. Representative absorption and desorption cycling data for the baseline MgH₂ powder (A and B) and for the SWCNT-MgH₂ nanocomposites (C and D). The cycling experiments were performed at 300 °C.

Figure 5. Absorption and desorption (4 wt % hydrogen) cycling data for the baseline MgH₂ powder and for the SWCNT-MgH₂ nanocomposites.

for 105 absorption/desorption cycles. However, that microstructure was not analyzed.

Figure 5 shows that the kinetics of the baseline powder rapidly deteriorate during cycling. By cycle 10, the baseline takes approximately twice as long to absorb and four times as long

to desorb as it did at the onset of testing. The SWCNT encapsulated powders not only sorb hydrogen at much higher rates but also maintain their stability for much longer times. For example, in the 35 cycled SWCNT-MgH₂ samples, the time to absorb doubles after 35 cycles rather than after 10.

Figure 6. Activation energy of desorption obtained via Kissinger analysis. The powder history and activation energy are given on the graph.

Similarly, in the SWCNT–MgH₂ powders, the time to desorb only increases by a factor of 2 after 35 cycles. The SWCNT–MgH₂ samples tested at 11 bar absorption and 0.04 desorption showed much improved kinetics compared to the 10 bar absorption and 0.1 bar desorption specimens. This agrees with the known significant dependence of the hydrogen sorption rates on the deviation from equilibrium plateau pressure.

Figure 6 shows desorption activation energy plots obtained from the Kissinger analysis. The testing conditions include powders analyzed directly after milling as well as post sorption cycled specimens. The activation energy of as-milled MgH₂ is in the same range as previously reported³⁶ and is approximately 20 kJ/mol lower than that of identical but unmilled powder. Comilling with the SWCNTs reduces the activation energy for desorption, implying a catalytic effect of the metal particle–nanotube combination. However, this roughly 25 kJ/mol reduction in the activation energy is rather modest compared to the previously reported 60 kJ/mol decrease due to the addition of advanced metallic catalysts such as V in large quantities (>10 wt %).³⁷

After 10 cycles, the activation energies for desorption in baseline MgH₂ and in the nanocomposite are nearly identical. After prolonged cycling, they all converge to the value for unmilled powder of roughly 150 kJ/mol.³⁶ This indicates a similarity in the desorption rate controlling steps despite a tremendous difference in the measured sorption times. The convergence of the activation energies also clearly indicates that any catalytic effect due to the metal nanoparticles is lost after prolonged sorption cycling.

Unfortunately, we do not have sufficient information regarding the absorption activation energy to make a significant comparison of hydrogenation versus dehydrogenation behavior. However, Figure 5 implies that starting at cycle 1 the nanocomposite microstructure does influence absorption more than desorption.

Figure 7 shows the grain size and lattice strain in the baseline and the nanocomposite materials as a function of cycle number. The data at zero cycles is for the as-milled powders prior to sorption testing. The grain size in both systems increases during cycling. Judging from the grain size values after 10 cycles, the nanocomposite coarsens slower than the baseline. This is not unexpected, since the kinetics of the SWCNT–MgH₂ system are faster, which in turn means that the composite spends less time at elevated temperature per sorption cycle. The two systems do not have significant differences in the lattice strain. This indicates that SWCNT coverage does not appreciably influence the strain in the hydride either during milling (cycle 0) or during subsequent sorption cycling.

Figure 7. Grain size and lattice strain versus cycle number for the baseline MgH₂ and for the SWCNT–MgH₂ nanocomposite.

Figure 8 shows histograms of the particle size distributions at various testing conditions. Approximately 500 particles were analyzed to generate each histogram. The size distributions were obtained directly from TEM analysis of the as-processed powders. The powders were not agglomerated and could be easily dispersed as a monolayer onto an amorphous carbon grid without incurring artifacts due to overlap. Figure 8A shows the particle size distributions for the as-milled baseline MgH₂ and for the SWCNT–MgH₂ nanocomposite. The two batches have similar particle sizes and analogous size distributions. This confirms a previous claim²² that any kinetic sorption enhancement obtained in the as-milled condition (not after cycling) is not due to a particle size variation between the baseline and the comilled powders.

It is not possible to obtain a size distribution for the baseline powders after cycling, since the powders are very heavily agglomerated or sintered. Agglomeration is defined as a decrease in the total particle surface area without a net densification of

Figure 8. TEM-obtained particle size distributions for the as-milled powders and for the sorption cycled MgH₂–SWCNT nanocomposites. It is not possible to analyze the postcycled baseline MgH₂ powder due to extensive sintering of the particles.

the powder compact. Sintering is defined as a net densification of a powder compact with a corresponding decrease in the surface area. It is impossible to separate the two mechanisms without performing densification experiments of powder compacts coupled to surface area analysis.

The SWCNT-covered MgH₂ did not agglomerate/sinter as drastically. Hence, the postcycled particle size distributions were readily obtainable. This is shown in Figure 8B, after 10 and 35 cycles. The mean particle size did increase from 246 nm in the as-milled state to 294 nm after 10 cycles, and to 369 nm after 35 cycles. There is also a notable jump in frequency for the 1–2 μm range particles. Because such particle sizes were barely present in the postmilled samples, we judge them to be evidence of some cycling-induced agglomeration. These agglomerates, however, represent a minority portion of the microstructure. Since the remaining portion of the distribution does not significantly change going from 10 to 35 cycles, we may also conclude that it is those agglomerates that drive much of the mean size increase.

Figure 9A shows a SEM micrograph of a typical cluster of agglomerated/sintered powder particles in the MgH₂ baseline samples after 10 cycles. The figure highlights the overall scale of the system after sorption cycling, which transforms from tens and one hundred nanometers to several micrometers. This dramatic size increase agrees with the established explanation regarding the reason for increased kinetic sluggishness of the metal hydride powders with prolonged high temperature sorption cycling.

Figure 9B shows a bright field TEM micrograph of several sintered hydride particles taken from the same batch. The

micrograph shows an interface where it appears that two initially separate hydride particles have sintered/agglomerated together. The interface shows classic sintering/agglomeration behavior with the two particles forming a “neck” (arrowed) surrounded by porosity (lighter circular regions on each side). TEM analysis of other samples from the same batch confirmed that they too consisted of several initially smaller hydride particles that have sintered/agglomerated together. The sintering/agglomeration causes a loss in the total surface area for a given volume for the hydride (metal) and an increase in the diffusion distance for the hydrogen.

After 10 sorption cycles, the hydride particles were too thick to allow for quantitative TEM analysis of bulk microstructural features. To perform quantitative characterization of the grains and defects found in cycled baseline powder, it was necessary to mechanically break up the particles. This was achieved via manual mortar and pestle grinding followed by sonication. These deagglomeration techniques were employed, since they are known not to affect the bulk microstructure except for introducing a minor amount of additional strain. It is important to point out, however, that the particle sizes shown in Supporting Information Figures S1 and S2 are not representative of the postcycled size distribution. The *bulk* α -MgH₂ microstructure in the SWCNT-covered hydride and the baseline powder was quite similar. While the average grain size in the SWCNT-covered powders was smaller than in the baseline, both systems are characterized by wide variations in the grain sizes from particle to particle. Some hydride particles consisted of one or several large α -MgH₂ crystallites. While the crystallites did occasionally contain defects such as twins or stacking faults, overall their number frequency was much lower than in the as-milled samples, implying that they were annealed out. Other hydride particles consisted of numerous truly nanoscale hydride grains. The selected area diffraction patterns (SADs) reflected this difference, some being single zone axis spot patterns while others being discontinuous ring patterns.

Figure 10 shows a SWCNT-covered hydride particle that is composed of relatively few (as evidenced by the SAD pattern) α -MgH₂ grains. This TEM specimen was of the nanocomposite that has received 20 sorption cycles. The two grains imaged in dark field (Figure 10B) were obtained by using the two adjacent strong 110 type α -MgH₂ reflections. The stronger one, corresponding to the larger more intense crystallite on the left, is labeled in Figure 10C. The grains imaged in Figure 10B show mottled (nonuniform, blocky) dark field contrast displayed in varying extent by all hydride grains. Such contrast was previously reported for highly deformed ionic minerals such as phyllosilicates,^{38,39} though its origin (dislocations vs beam damage) is still debatable.

Figure 11 shows an example of unadsorbed metallic magnesium present in the SWCNT-covered powder. This sample was analyzed after the 20th absorption cycle. With prolonged cycling, the baseline MgH₂ powders displayed more metallic magnesium after absorption, agreeing with the volumetric results. Interestingly, we did not find any evidence of partially sorbed grains. Rather, the situation seemed binary; particles were either fully hydrided or not at all. The metallic magnesium shows fundamentally different contrast compared to the hydride, and is readily distinguishable. The vertically aligned defect beginning directly below the arrow and strongly visible in dark field is either a grain boundary or a dislocation. The particular crystallite(s) imaged in Figure 11B is near the $[-110]$ zone axis. The continuous rings visible in the SAD are not surprising and

Figure 9. (A) Scanning electron micrograph of several agglomerated/sintered MgH_2 particles after 10 cycles. (B) Bright field TEM micrograph of several sintered MgH_2 particles representative of the size distribution found in the baseline MgH_2 after 10 cycles. Arrows point to the sintered interface between two previously separate particles.

Figure 10. TEM micrographs highlighting $\alpha\text{-MgH}_2$ crystallites in the SWCNT- MgH_2 nanocomposite after 20 sorption cycles: (A) bright field micrograph; (B) dark field micrograph obtained using a $g = 110$ $\alpha\text{-MgH}_2$ reflection; (C) corresponding selected area diffraction (SAD) pattern.

Figure 11. TEM micrographs highlighting unsorbed Mg particles in the SWCNT- MgH_2 nanocomposite after 20 sorption cycles: (A) bright field micrograph; (B) dark field micrograph obtained using a $g = 200$ Mg reflection; (C) corresponding indexed selected area diffraction (SAD) pattern.

are from the oxide that always forms on the magnesium surface when exposed to even minuscule quantities of air or water vapor.

Figure 12 demonstrates how the carbon allotrope-metallic nanoparticle mixture still covers the hydride particles even after 35 cycles. Figure 12A shows a bright field STEM micrograph of the powder adjacent to a portion of the holey carbon grid holding the powder (holey carbon grids were used for analytical work, so as to eliminate the carbon background signal). Figure 12B shows the same area in Z-contrast high angle annular dark field (HAADF) mode. The region that is squared was analyzed

using EDXS elemental mapping. The brighter region in Figure 12B is revealed in Figure 12C to be a Ni-Co nanoparticle. The elemental maps shown in Figure 12C highlight that the carbon coats the MgH_2 quite uniformly and completely. The dark region in the carbon map in between the hydride particle and the holey carbon grid indicates that the background carbon signal is negligible. Since EDXS provides no structural information, it is unclear whether the metallic particles are reacted with the magnesium to form alloys or intermetallics. Additional site-specific electron diffraction analysis would be necessary to

Figure 12. (A and B) Z-contrast HAADF STEM micrographs of a metallic nanoparticle on the composite powder surface after 35 cycles. (C) EDXS elemental maps of carbon, magnesium, cobalt, and nickel in the area marked by a red square.

Figure 13. Raman spectra of the SWCNT–MgH₂ nanocomposites before and after cycling, indicating that the SWCNTs have survived 35 absorption/desorption cycles.

answer that question. However, it is known from the activation energy analysis (Figure 6) that all catalytic effects are lost after sorption cycling, implying that the particles did react.

Figure 13 shows the Raman spectra of the as-milled SWCNT-covered hydride obtained directly after comilling and after 35 sorption cycles. In the spectra, the G-band is representative of the c-c graphite bonds and the D-band is representative of the defects in the structure of carbon nanotubes. The spectra demonstrate that the defective (due to the ball milling) SWCNTs survive the sorption cycling without any additional noticeable degradation. Even after 35 cycles, the SWCNTs still coat the hydride surface, preventing sintering and agglomeration.

Discussion

To summarize, the main and arguably only difference between the two samples' postcycled *bulk* microstructures is the average

grain size. We believe that this is due to the variation in the time spent at elevated temperature per sorption cycle for the nanocomposite versus the baseline MgH₂ powders. However, these differences are not that large and cannot be responsible for the sorption kinetics variation. As was shown in the Results, sorption cycling causes the activation energy of desorption in the nanocomposite and in the baseline MgH₂ to converge to a value of roughly 150 kJ/mol.

The MgH₂ to Mg phase transformation is still debatable. Several rate-limiting mechanisms have been proposed: (1) the high activation energy of hydrogen dissociation/reassociation on the MgH₂ surface;⁴⁰ (2) the slowness of the Mg–MgH₂ phase boundary movement due to the slow diffusivity of the hydrogen ions primarily through the hydride but also perhaps through the metal;^{41–45} (3) the diffusion of hydrogen along a metal–MgH₂ interface.^{46,47} In addition, some have argued that surface passivation/poisoning due to adsorbed oxygen or sulfur-containing species may also be rate limiting.⁴⁸ Attempting to ascribe specific rate-limiting mechanisms that correspond to measured activation energies may not be that fruitful. A 150 kJ/mol activation energy for desorption may be attributed to any one of the above mechanisms. For example, it is well-known that the activation energy for hydrogen recombination on the pure α-MgH₂ surface is relatively high. The literature-quoted values include 144 and 172 kJ/mol (see ref 40 and the citations therein). Alternatively, an activation energy of 160 kJ/mol was recently reported to coincide with hydrogen diffusion through the α-MgH₂ phase being the rate-limiting step in desorption.⁴⁹ Moreover, recent modeling work also indicates that because of the interdependence of hydrogen diffusion and dissociation mechanisms a single rate-limiting step may not exist at all.⁵⁰

What does vary by orders of magnitude between the baseline and the SWCNT-covered powder is the particle size. Without any additional catalytic enhancement, such a difference in the particle size will translate into a tremendous change in the time required to achieve a certain level of absorption/desorption. This is true both in terms of mechanism 1, i.e., the surface to volume ratio, and in terms of mechanisms 2 and 3, i.e., the diffusion distances. Considering the latter, we can obtain a rough estimate of the effect of particle size on sorption times through the well-known shrinking core model.^{51,52} The model, which assumes a diffusion-controlled reaction, relates the fraction of material reacted f to the time t and the average particle radius of the reactant R . The difference in the rates of hydrogen diffusion through the metallic magnesium versus MgH_2 phases is incorporated into the rate constant k , such that $k_{\text{desorption}} \neq k_{\text{absorption}}$. The most general form of the relationship is the following: $(1 - f^{1/3}) = 1 - kt^{1/2}/R$. This can be rearranged to provide an expression for the time to achieve a constant amount of sorption: $t = R^2(1 - (1 - f^{1/3}))^2/k^2$. The formula highlights the strong dependence of diffusion-controlled kinetics on the particle size and indicates why a secondary phase that coats the hydride and prevents particle sintering/agglomeration is so beneficial. For example, a change in a particle diameter from 200 nm to 2 μm will result in 2 orders of magnitude increase in the time to react.

An implication of this work regards the possibility of stabilizing the nanoscale size of a variety of hydrogen chemisorbing materials during elevated temperature sorption cycling. While numerous routes have been found to achieve initially nanoscale dimensions, very few routes, such as melt infusion into a porous matrix host, exist to preserve this structure at elevated temperatures after tens or hundreds of hydrogenation/dehydrogenation cycles. We have now shown that another, perhaps simpler route is available to achieve a similar result. High-energy milling is a well-established technique to reduce the particle size of powders or to achieve an intimate mixture of several phases. Workers who comill hydrides with carbon nanotubes recognized this method as a very good way to disperse the two phases but did not fully appreciate the implication for size stabilization. The SWCNT–amorphous carbon mixture is now shown to work, presumably due to the high structural and chemical stability and fine size of the nanotubes. However, other nanodispersed carbon allotropes may be similarly effective and will be explored in future cycling studies.

Conclusions

In this study, we detailed the hydrogen sorption cycling performance of SWCNT–magnesium hydride nanocomposites. A nanocomposite microstructure was achieved through high energy comilling the hydride along with a mixture of SWCNTs, amorphous carbon, and metallic nanoparticles. The nanocomposite and identically milled baseline MgH_2 (baseline) were volumetrically sorption cycled at 300 °C. The SWCNT-covered MgH_2 displays a fundamentally different sorption cycling behavior compared to the baseline, though the activation energies for desorption are roughly identical. The kinetics of the baseline powder rapidly degrade, where by sorption cycle 10 it takes nearly 84 min to absorb 4 wt % hydrogen and over 6 h to desorb this quantity. Conversely, the nanocomposites display much improved kinetic stability. At cycle 10, the time to absorb 4 wt % hydrogen is 7 min, while the time to desorb is 80 min. Even at cycle 35, the time to absorb is only 14 min, while the time to desorb is 2 h. A more aggressive (in terms of

variation of the sorption pressure from the plateau pressure) sorption regime allowed SWCNT-covered MgH_2 to be tested up to 105 absorption desorption cycles with only minor kinetic degradation.

TEM analysis confirms that nanocomposite microstructure stabilizes the MgH_2 particle size during cycling. At the onset of cycling, the mean diameters of the SWCNT-covered hydride and of the baseline are 246 and 220 nm, respectively. After 10 cycles, the baseline MgH_2 powders sinter/agglomerate, becoming micrometers in scale. However, the mean diameter of the SWCNT-covered particles increases to only 294 nm after 10 cycles, and to 369 nm after 35 cycles. TEM analysis and Raman spectroscopy confirm that even after 35 cycles the hydride particles remain covered by the SWCNTs and by the amorphous carbon.

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Supporting Information Available: Figure S1 highlights a large hydride grain in the postcycled baseline sample that contains stacking faults (arrowed). Figure S2 highlights the other type of grain distribution commonly found in the powders. Figure S2 shows TEM micrographs of numerous truly nanocrystalline $\alpha\text{-MgH}_2$ grains present in the baseline MgH_2 even after 10 cycles. The size of the hydride crystallites varies quite significantly, though many particles are in the same 20 nm range as confirmed by XRD analysis. Figure S2 demonstrates that despite sorption cycling the microstructure does remain nanocrystalline. Rather, it is the particle size that evolves the most. Figure S3 highlights a 200 nm scale $\alpha\text{-MgH}_2$ crystallite present in the SWCNT-covered hydride after the sample was cycled 35 times. The dimensions of this crystallite are representative of the average scale of the microstructure. The smaller crystallites visible in the dark field micrograph are from the surface oxide and are associated with the continuous rings in the SAD pattern that inevitably get captured by the objective aperture. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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