Microwave irradiation effects on reversible hydrogen desorption in sodium aluminum hydrides (NaAlH₄)

Rahul Krishnan a, Dinesh Agrawal b, Tabbetha Dobbins a,c,∗

a Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA 71272, USA
b Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA
c Department of Physics, Grambling State University, Grambling, LA 71245, USA

A R T I C L E   I N F O

Article history:
Received 17 October 2007
Received in revised form 5 February 2008
Accepted 11 February 2008
Available online 1 April 2008

Keywords:
Metal hydrides
Amorphization
Dielectric response
X-ray diffraction

A B S T R A C T

The effect of microwave irradiation on the reversible desorption reaction in sodium aluminum hydride (NaAlH₄) is explored. NaAlH₄ is doped with 2 mol% TiCl₂ and pre-activated by high energy ball milling and aging to show the presence of metallic aluminum phase. As a catalyst, Ti²⁺ has been used to improve desorption kinetics in sodium alanate. X-ray diffraction was performed on the samples exposed to microwave irradiation for 10, 20, 30, 40 and 50 min. Results show that when the powders show the presence of aluminum, a steady increase in the formation of the hexahydride (Na₃AlH₆) phase and Al occurs during microwave irradiation; and is accompanied by a steady reduction in the NaAlH₄ phase XRD peak (hkl) intensities. This data suggests that microwave irradiation drives the reversible H₂ desorption reaction in NaAlH₄. NaAlH₄ doped with 2 mol% TiCl₂ which does not show the presence of Al phase, undergoes a reduction in NaAlH₄ peak intensities with increasing microwave exposure (and no reversible product phases are detected in this case). Dielectric studies on NaAlH₄ indicate that microwave penetration is low. Therefore, it is proposed that microwave irradiation heating of the Al particulate phase is responsible for the hydrogen desorption reaction pathway which is similar to that of conventional heating.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Sodium aluminum hydride (NaAlH₄) has a crystalline structure wherein Al³⁺ is tetrahedrally coordinated by H⁻ anions. Upon heating (to ~186 °C), H₂ gas is liberated in a reversible reaction making NaAlH₄ a viable candidate for on-board hydrogen storage [1–4]. The reversible hydrogen storage reaction has been well studied since its discovery by Bogdanovic and Schwickardi [1] in 1997. The desorption of H₂ from NaAlH₄ occurs by the two step reaction as follows:

\[
\text{NaAlH₄} \rightarrow \text{Na₃AlH₆} + \frac{2}{3} \text{Al} + \frac{2}{3} \text{H₂} \quad \text{(step 1)}
\]

In past few years, microwave processing of materials has realized many successes due to its rapid heating characteristics and non-thermal effects. Roy et al. have shown the advantage of microwaves over conventional heating in several studies, and have demonstrated the decrystallization of oxides under the effect of electric and magnetic microwave fields [5]. Microwaves can heat different states of matter to high temperatures in less time and produce superior sintered products, with higher densities and smaller grain sizes, compared to those processed by conventional heating. Presently, microwave processing is the most viable option for sintering of powders into highly dense bodies within minutes [6]. Additionally, researchers in the area of microwave processing of materials project efficient heating profiles with lower energy cost [7]. Sato et al. calculated the energy consumption for sintering traditional ceramics to 100% theoretical density using a microwave furnace and compared those values to the energy consumption for performing the same operations in a conventional furnace. Table 1 compares processing time and energy consumption of microwave versus conventional gas kilns. The microwave furnace achieved 100% theoretical density using one-fifth of the energy (kWh) relative to the conventional furnace. The main reason for the reduction in energy consumption in microwave furnaces is the reduced processing time [8]. The reaction pathways under microwave irradiation may be dramatically different compared to those driven by conventional processes. The rapid heating caused by microwave irradiation could also result in bypassing of certain intermediate product phases [9].

Recently, Nakamori et al. published a study of the dehydrogenation of some metal hydrides (LiH, NaH, MgH₂, CaH₂ and TiH₂) and alkali borohydrides (LiBH₄, NaBH₄ and KBH₄) via microwave irradiation [10]. It has been shown that microwave processing...
does drive the dehydrogenation process. However, in those experiments, microwave treatment tends to drive the metal hydrides into an amorphous state [10]. Fang et al. have reported a higher degree of microwave enhancement on the sintering properties of amorphous phases in alumina above enhancements observed in stable crystalline phases [11]. The Fang et al. study would suggest that microwaves couple more readily to disordered structures relative to ordered structures. In fact, microwaves may drive order-to-disorder reactions due to this coupling. For metal hydrides, loss of crystallinity under microwave treatment will affect the reversible nature of the desorption reaction, which is highly essential for on-board vehicular hydrogen storage applications. The work presented here reveals the processing conditions for the formation of reversible product phases after first step of the desorption reaction in NaAlH4 driven using microwave irradiation.

2. Experimental procedure

For this study, sodium aluminum hydride (Sigma–Aldrich 90% technical grade) and titanium (II) chloride (Sigma–Aldrich 99.98% pure) were used. Mixtures of NaAlH4 and 2 mol% TiCl2 were prepared by high energy ball milling (HEBM) (SPEX Certiprep 8000M Miller) for 25 min, using tungsten carbide (WC) milling media and mill jar. One batch of the TiCl2 catalyzed NaAlH4 starting powder was prepared by HEBM only (called Batch 1), while the other was aged for 2 weeks in a dry N2 glove box after HEBM until it showed the presence of metallic Al. The sample containing the metallic Al is said to be ‘pre-activated’ (and is called Batch 2). The ratio of the mass of the milling media to the mass of the powder was maintained at 1.25. For microwave experiments, 0.2 g of the starting mixture was loaded into small vials within a glove box and the vials were sealed under dry nitrogen atmosphere to prevent exposure of powders to air. Samples from Batch 1 and Batch 2 were processed using a 2 kW/2.45 GHz multi mode microwave furnace. Batch 1 was microwave treated for 30 and 60 min. Batch 2, the Al pre-activated NaAlH4, was microwave treated for 10, 20, 30, 40 and 50 min. After microwave irradiation, the samples were characterized by X-ray diffraction (Rigaku Miniflex) to determine the product phases. Cu Kα (1.54 Å) radiation was used. The step size for the scans was fixed at 0.1° (2θ) while the scan rate was 4°/min. MDI Jade (Version 6.5.23) was used to analyze the X-ray diffraction data. Dielectric measurements were conducted on non-catalyzed, inactivated NaAlH4 using HP 8510 Network Analyzer (Materials Research Laboratory, Pennsylvania State University). NaAlH4 was packed into a coaxial cable. The input port (Port 1) of the network analyzer was connected at one end of the coaxial cable while the output port (Port 2) at the other end. In transmission mode, input is given at Port 1 and the output is also measured at Port 1 (S11). Both modes were used for this study. Residual gas analysis (RGA) was performed on the microwave treated samples at 10, 20, 30, 40 and 50 min using a Stanford Research Systems QMS 200 Gas Analyzer.

3. Results and discussion

The dielectric loss of pure NaAlH4 in a 2.45 GHz microwave field is not sufficient to drive the dehydrogenation reaction. Measurements show that the real permittivity of undoped NaAlH4 is 4.077 while the loss factor is very low (1.16 × 10^-3). Fig. 1 gives the transmission and reflection losses on a logarithmic scale as a function of frequency ranging from 0 to 18 GHz. Negligible transmission losses indicate that microwave range frequencies can pass from Port 1 straight through NaAlH4 to Port 2 without being absorbed by NaAlH4. Reflection losses are relatively higher because of surface conduction in NaAlH4, which is responsible for losses in the signal measured at Port 1. From these results, it is clear that the penetration of microwaves into pure NaAlH4 is poor. When samples of pure NaAlH4 are exposed to microwave radiation, no measurable weight loss was observed, i.e. no hydrogen is desorbed after the exposure. Therefore, the metal hydride samples were catalyzed with TiCl2, a known catalyst for the dehydrogenation reaction [1–4,12] and, also, a material with moderate dielectric loss properties.

As mentioned earlier, one batch of catalyzed NaAlH4 did not contain metallic Al phase in the precursor material (Batch 1). The X-ray diffraction patterns collected from Batch 1 powders are given in Fig. 2 for untreated, microwave treated for 30 min and microwave treated for 60 min samples. On exposure to microwaves for 30 and 60 min, no peaks corresponding to Na3AlH6 or Al are observed. However, the NaAlH4 peak intensities steadily decrease with increasing microwave exposure time. This decrease in NaAlH4 peak intensity is likely due to amorphization of the NaAlH4 lattice. The NaAlH4 peak at 2θ = 29.7°, which is the strongest intensity NaAlH4 peak, reduces in intensity with increasing microwave exposure time. The less intense peaks ranging between 2θ = 74° and 2θ = 79° near disappear completely after microwave exposure. These results are consistent with data reported by Nakamori et al. [10] wherein the amorphization of LiBH4 is observed. Microwave treatment tends to cause loss in long range periodicity thus making the hydrides amorphous. This amorphization is a disadvantage to the deployment of microwave desorption from hydrides for systems where reversibility is a requirement. A strategy where a susceptor material, which heats readily upon microwave exposure, is included may improve the outlook for reversibility after microwave exposure. This is the case for Batch 2 powders (which contain metallic Al).

In order for microwave processing to impact hydrogen storage, it is imperative to identify reversible dehydrogenation compounds, such as Na3AlH6 and Al, to confirm that microwave exposure is facilitating the reversible desorption reaction first reported by Bogdanovic and Schwickardi [11]. Fig. 3 shows the phase progression in Batch 2 after different irradiation times—0, 10, 20, 30, 40 and 50 min. The samples are labeled as UnMW, MW_10, MW_20, MW_30, MW_40 and MW_50, respectively. Batch 2 powders were comprised of NaAlH4 pre-activated with metallic Al. XRD analysis of the untreated sample (i.e. UnMW) (Batch 2) shows NaAlH4.
Fig. 2. X-ray diffraction pattern for Batch 1 powders (NaAlH₄ not activated with metallic Al). Shown inset is the intensity reduction in the NaAlH₄ peak at 2θ ~ 29.6° with microwave exposure times of 30 and 60 min. This peak intensity undergoes reduction with more time of microwave exposure.

and Al (Fig. 3). Na₃AlH₆ is also a decomposition product of NaAlH₄. However, in trace amounts it is not detected by XRD. In general, a minimum of 1 vol.% of a phase is required for its detection by XRD. Trace amounts of Al are detected while Na₃AlH₆ are not detected by XRD because Na has a lower electron density than Al and since Na is the primary constituent in the hexahydride phase, the diffraction peak intensity from this phase is diminished below background. The work of Anton [12] showed that ball milling of as-received NaAlH₄ activates or partially dehydrogenates it. Gross et al. [4] showed that NaAlH₄ doped with 9 mol% of TiCl₃, when milled for 3 h, results in the partial (%) decomposition of NaAlH₄ into Na₃AlH₆ and Al. HEBM and aging for 2 weeks activates our samples leading to the appearance of the Al decomposition phase. XRD data for the untreated sample (called UnMW) contains peaks that correspond to NaAlH₄ and two peaks at 2θ values of 38.602° and 44.811° corresponding to metallic Al. Ball milling also reduces the particle size in most powder systems and these particle size effects may also have an effect on the ability of materials to couple with microwaves. Lorenson and co-workers [13] studied the effect of particle size on the ability of carbon to absorb microwave heat and demonstrated...
that the heating rate decreases with an increase in particle size. The Maxwell–Wagner model [14] describes the relaxation time in a capacitor with a two-layer dielectric. The relaxation time ($\tau$) is a function of the permittivities ($\varepsilon_1, \varepsilon_2$), conductivities ($\sigma_1, \sigma_2$) and the dimensions ($d_1, d_2$) of the two layers and is given by

$$\tau = \frac{\varepsilon_1 d_2 + \varepsilon_2 d_1}{\sigma_1 d_2 + \sigma_2 d_1}$$  \hspace{1cm} (2)

Based on the Maxwell–Wagner model, we can infer that for a given material with given permittivity, conductivity and dimensions, penetration will be best at lower microwave frequencies. Otherwise, it may be possible to achieve good penetration at higher frequencies by reducing the particle size i.e. affecting $d_1$ and $d_2$. Thus, in the case of hydrides, it is expected that reduction of the particle size will result in greater polarizability, higher dielectric constant and thus more microwave penetration into the bulk of particles.

To quantify phases driven by the reaction, we have performed a relative peak intensity analysis (reported in Table 2). Two NaAlH$_4$ peaks ($2\theta \sim 30^\circ$ and $2\theta \sim 60^\circ$), two Na$_3$AlH$_6$ peaks ($2\theta \sim 32^\circ$ and $2\theta \sim 58^\circ$) and two Al peaks ($2\theta \sim 39^\circ$ and $2\theta \sim 45^\circ$) were chosen for this analysis. The ratios of the peak intensities of Na$_3$AlH$_6$ to NaAlH$_4$ and Al to NaAlH$_4$ were calculated for each pattern. As the reaction proceeds, it is expected that the intensity ratios should increase because Na$_3$AlH$_6$ and Al should increase in quantity and NaAlH$_4$ should decrease as the reaction proceeds with microwave exposure. These ratios increase with increasing microwave time showing that the desorption process continues over the duration of microwave exposure. NaAlH$_4$ peaks at $2\theta \sim 30^\circ$ and $2\theta \sim 60^\circ$ vary from 100% to 28.1% intensities, respectively, in the untreated sample (UnMW) pattern to 0% in MW$_{40}$ and MW$_{50}$. Na$_3$AlH$_6$ ($2\theta \sim 58^\circ$ and $2\theta \sim 32^\circ$) has 0% intensity in UnMW, but its intensity increases progressively with irradiation time to reach 93.9% and 27.6%, respectively in MW$_{50}$. Al peaks ($2\theta \sim 39^\circ$ and $2\theta \sim 45^\circ$) vary from 34.5% to 15.4% intensity in control sample (i.e. UnMW) to 100% and 50.5% in MW$_{50}$. Whenever the NaAlH$_4$ peaks diminish to zero intensity, the peak intensity ratio goes to infinity, as indicated by $\infty$ in Table 2. This data confirms that NaAlH$_4$ is gradually converted into Na$_3$AlH$_6$ and Al releasing hydrogen by the reversible dehydrogenation reaction of step 1 in Eq. (1). Relatively small NaAlH$_4$ peaks at $2\theta = 51.6^\circ, 55^\circ, 60.5^\circ, 61.8^\circ, 75.8^\circ$ have all diminished in successive diffraction patterns with increasing irra-

---

**Fig. 3.** X-ray diffraction patterns for Batch 2 powders which were pre-activated with metallic Al. XRD patterns are arranged in order of increasing time of microwave exposure. The symbols in the last pattern indicate presence of Na$_3$AlH$_6$ and Al phases only. At longer microwave exposure times (40 and 50 min) Na$_3$AlH$_6$ and Al product phases exist while NaAlH$_4$ peaks are absent.
the two NaAlH₄ peaks in the UnMW pattern. At close inspection, the MW₂₀, MW₃₀, MW₄₀ and MW₅₀ samples contain a very low intensity X-ray peak at 2θ = 77.9° corresponding to this line. At the longest exposure times, the NaAlH₄ peaks all disappear and the sample exhibits peaks corresponding to only Na₃AlH₆ and Al phases.

Table 2 contains gravimetric analysis data (weight loss) for Batch 2 powders microwave treated for 10, 20, 30, 40 and 50 min. In all cases, the initial sample weight was 0.2 g. An increase in weight loss during microwave exposure is observed. Fig. 4 shows this trend graphically (in terms of hydrogen loss). Fig. 5 shows residual gas analysis (RGA) for hydrogen desorbed from the sample during microwave exposure. The hydrogen composition (%)) is relative to the hydrogen content in the gas stream of the measurement assembly apparatus feed lines, which included N₂ and H₂O. Hydrogen was determined using 2X repeated measurements). Standard deviation on the measurement process is ±0.00014 g (determined using 2X repeated measurements).

Two phenomena are observed during the exposure of TiCl₂ doped NaAlH₄ to microwave irradiation. In Batch 1 powders, metallic Al phase is absent from the starting powders or the untreated sample. These samples show a tendency to lose crystalline nature (amorphize) on exposure to microwave radiation. The electromagnetic field in the microwave furnace tends to transform the metal hydride from a stable crystalline phase to a thermodynamically unstable amorphous phase [11]. This is consistent with results shown by Nakamori et al. [10] wherein hydride powders become amorphous upon microwave exposure. In those studies, the desorption reaction efficiency is increased after microwave driven dehydrogenation [10]. Batch 2 on the contrary shows the presence of metallic Al phase in the untreated sample. Here, we clearly detect the reversible product phases of Na₃AlH₆ and Al. Amounts of those phases increase with increasing microwave exposure time.

development time. At 2θ = 77.9°, a line marker for Na₃AlH₆ falls between the two NaAlH₄ peaks in the UnMW pattern. At close inspection, the MW₂₀, MW₃₀, MW₄₀ and MW₅₀ samples contain a very low intensity X-ray peak at 2θ = 77.9° corresponding to this line. At the longest exposure times, the NaAlH₄ peaks all disappear and the sample exhibits peaks corresponding to only Na₃AlH₆ and Al phases.

Table 2 contains gravimetric analysis data (weight loss) for Batch 2 powders microwave treated for 10, 20, 30, 40 and 50 min. In all cases, the initial sample weight was 0.2 g. An increase in weight loss during microwave exposure is observed. Fig. 4 shows this trend graphically (in terms of hydrogen loss). Fig. 5 shows residual gas analysis (RGA) for hydrogen desorbed from the sample during microwave exposure. The hydrogen composition (%)) is relative to the hydrogen content in the gas stream of the measurement assembly apparatus feed lines, which included N₂ and H₂O. Hydrogen was determined using 2X repeated measurements). Standard deviation on the measurement process is ±0.00014 g (determined using 2X repeated measurements).

Two phenomena are observed during the exposure of TiCl₂ doped NaAlH₄ to microwave irradiation. In Batch 1 powders, metallic Al phase is absent from the starting powders or the untreated sample. These samples show a tendency to lose crystalline nature (amorphize) on exposure to microwave radiation. The electromagnetic field in the microwave furnace tends to transform the metal hydride from a stable crystalline phase to a thermodynamically unstable amorphous phase [11]. This is consistent with results shown by Nakamori et al. [10] wherein hydride powders become amorphous upon microwave exposure. In those studies, the desorption reaction efficiency is increased after microwave driven dehydrogenation [10]. Batch 2 on the contrary shows the presence of metallic Al phase in the untreated sample. Here, we clearly detect the reversible product phases of Na₃AlH₆ and Al. Amounts of those phases increase with increasing microwave exposure time.

Table 2

<table>
<thead>
<tr>
<th>Ratio of product: reactant</th>
<th>X-ray diffraction intensities</th>
<th>Sample weight loss (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlH₄ (2θ ~ 32°)</td>
<td>NaAlH₄ (2θ ~ 30°)</td>
<td>NaAlH₄ (2θ ~ 58°)</td>
</tr>
<tr>
<td>NaAlH₄ (2θ ~ 60°)</td>
<td>NaAlH₄ (2θ ~ 30°)</td>
<td>NaAlH₄ (2θ ~ 39°)</td>
</tr>
<tr>
<td>MW₀</td>
<td>0</td>
<td>0.015</td>
</tr>
<tr>
<td>MW₁₀</td>
<td>0.433</td>
<td>0.154</td>
</tr>
<tr>
<td>MW₂₀</td>
<td>2.198</td>
<td>0.475</td>
</tr>
<tr>
<td>MW₃₀</td>
<td>14.206</td>
<td>1.205</td>
</tr>
<tr>
<td>MW₄₀</td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>MW₅₀</td>
<td>∞</td>
<td>∞</td>
</tr>
</tbody>
</table>

These ratios are increasing with increasing microwave exposure time due to formation of Na₃AlH₆, Al and consumption of NaAlH₄. Also indicated is the weight loss in each sample. The initial weight of all samples was 0.2 g. The theoretical weight loss for H₂ liberated from the 0.2 g samples in step 1 of the NaAlH₄ decomposition reaction is 0.0074 g.

![Fig. 4](image1.png)

Fig. 4. Samples weight loss as a function of increasing microwave exposure time. An upward trend in weight loss is seen. The horizontal at 0.0074 g indicates the theoretical hydrogen weight loss for the 0.2 g samples used in this study. Standard deviation on the measurement process is ±0.00014 g (determined using 2X repeated measurements).

![Fig. 5](image2.png)

Fig. 5. Residual gas analysis (RGA) showing the composition (%) of liberated H₂ at 30, 40 and 50 min relative to other gases (e.g. N₂, H₂O, CH₄ and O₂) in the measurement assembly.
Possibly, under the microwave irradiation, the metallic Al phase couples to microwave irradiation to produce sample heat up resulting in increased atom mobility in the NaAlH4 phase—an effect that would tend to counter a microwave driven amorphization reaction in the NaAlH4 phase. This, in turn, could drive the desorption reaction of NaAlH4 with a reaction pathway similar to that observed under conventional heating conditions. Detection of reversible product phases in a microwave driven reactions is key to ensuring reversibility in microwave irradiation driven desorption processes.

Another interesting phenomenon observed in these studies is the splitting of NaAlH4 peaks after microwave treatment. This possibly indicates strain in the NaAlH4 lattice structure. This lattice strain may be related to the diffusion of hydrogen out of the lattice. This residual strain may also indicate onset of amorphization of the NaAlH4 crystalline phase by microwave irradiation. Doublet peaks or splitting of the peaks [15] in the NaAlH4 phase are a common phenomenon observed among the microwave treated samples from Batch 2. This could be attributed to residual stress in the crystallographic structure of NaAlH4 due to atom vibrations influenced by microwave irradiation. The second peak in the NaAlH4 structure reveals at a decreased lattice parameter, indicating that the crystal may have undergone loss of interstitial H− (i.e. H2 desorption) without structure transformation to Na3AlH6 and Al.

4. Conclusions

Microwave assisted dehydrogenation of NaAlH4 doped with 2 mol% TiCl2 has been carried out in the absence (Batch 1) and presence (Batch 2) of metallic Al phase in the starting material. Microwave exposure of Batch 1 resulted in NaAlH4 becoming amorphous. Presence of metallic Al in the untreated sample (Batch 2) shows the reversible product phases, Na3AlH6 and Al on microwave exposure. The presence of these phases confirms the reversible nature of sodium aluminum hydride under microwave assisted dehydrogenation. Further research is needed to understand the thermodynamics and kinetics of the microwave assisted dehydrogenation reactions. The condition for retention of crystalline nature of other metal hydrides under microwave irradiation is also worth exploring in future studies. This will determine the conditions for which microwave irradiation can be used as a dehydrogenation/processing technique to achieve higher levels of energy efficiency for on-board hydrogen storage systems. Ultimately, energy efficiency through the use of microwaves may be addressed and may result in a new technology for on-board vehicle hydrogen storage applications. Future work will also include microwave assisted hydrogen absorption on NaAlH4 to further test the viability of these systems in cyclic applications.

Acknowledgements

Funding for this project was provided by the Department of Energy, Office of Basic Energy Sciences (Contract No.: DE-FG02-05ER46246). We would also like to acknowledge staff at the Institute for Micromanufacturing (IfM) (Ruston, LA) and the Materials Research Institute (University Park, PA) for their support. We thank Larry Hurtt for his valuable insights into this project through personal discussions.

References