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# Investigation of dehydrogenation mechanism of MgH2-Nb nanocomposites

J. Huot<sup>a,\*</sup>, J.F. Pelletier<sup>b,1</sup>, L.B. Lurio<sup>c,2</sup>, M. Sutton<sup>b</sup>, R. Schulz<sup>a</sup>

<sup>a</sup>Chimie et matériaux, Institut de recherche d'Hydro-Québec, Varennes, Québec, Canada J3X 1S1 <sup>b</sup>Centre for the Physics of Materials, McGill University, Montréal, Québec, Canada H3A 2T8

<sup>c</sup>Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

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## Abstract

Nanocomposites of composition  $MgH_2-V$  and  $MgH_2-Nb$  have been shown to have very fast hydrogen sorption kinetics. This could be explained by the presence of vanadium, which eases hydrogen penetration into the material, and by the particular microstructure of this nanocomposite. In this paper, we report a systematic structural study of the nanocomposite  $MgH_2-Nb5at.\%$ . To see the effect of hydrogenation/dehydrogenation process on the crystal structure, X-ray diffraction under hydrogen pressure was carried out at different temperatures. Crystallite size was evaluated by X-ray powder diffraction peak broadening. In order to see the evolution of crystal phases during the dehydrogenation process, real time X-ray investigation of dehydrogenation in  $MgH_2-Nb$  nanocomposite was carried out using synchrotron radiation. It was found that a niobium hydride metastable phase, closely related to the low temperature  $\varepsilon$ -NbH phase, acts as a gateway for hydrogen. Activation energies of the hydrogenation and dehydrogenation processes are also estimated. © 2002 Elsevier Science B.V. All rights reserved.

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# 1. Introduction

Magnesium hydride is a promising candidate for hydrogen storage applications. It is a lightweight and low-cost material with high hydrogen storage capacity. However, the hydrogen sorption takes place at a high temperature and with slow kinetics. Recently, it has been shown that milling magnesium or magnesium hydride with a transition metal leads to the formation of a nanocomposite structure with excellent hydrogen sorption kinetics [1-4]. In particular, when the transition element forms a hydride, for example in the system  $MgH_2+5at.\%V$ , the resulting nanocomposite shows very good sorption kinetics [2,3,5]. For the system  $MgH_2+5at.\%V$ , the dehydrogenation ratelimiting steps in this nanocomposite have also been investigated [5]. In a previous paper [6], we have shown that for the MgH<sub>2</sub>-Nb nanocomposite, a metastable phase of approximate composition NbH<sub>0.6</sub> appears during the dehydrogenation process and may act as a gateway for hydrogen flow.

In the present paper, we report further investigation on the dehydrogenation mechanism in  $MgH_2+5at.\%Nb$ nanocomposite. In-situ X-ray powder diffraction and timeresolved X-ray scattering using synchrotron radiation were used to follow structural changes during dehydrogenation. The high-brightness of synchrotron X-ray sources combined with a fast linear detector made it possible to acquire diffraction patterns covering 20° as fast as every 5 ms. Therefore, even the rapid sorption kinetics of nanocomposite Mg-based materials could be probed in real-time.

# 2. Experimental details

Magnesium hydride from Th. Goldschmidt (95wt.%  $MgH_2$ , 5wt.% Mg) and 5at.% of niobium powder (Cerac, 99.9% pure) were mixed inside an argon-filled glove box. The mixture was milled for up to 20 h in a Spex 8000 model shaker mill using a vial and balls of stainless steel with a ball to powder weight ratio of 10:1. In a previous paper, it was reported that in  $MgH_2+5at.$ % Nb nanocomposite, niobium is evenly distributed in the magnesium matrix with an average particle size of 63 nm [7].

<sup>\*</sup>Corresponding author.

E-mail address: jhuot@ireq.ca (J. Huot).

<sup>&</sup>lt;sup>1</sup>Present address: Visual Systems Engineering, CAE Inc., St-Laurent, Québec, Canada H4L 4X4.

<sup>&</sup>lt;sup>2</sup>Present address: Department of Physics, Northern Illinois University, DeKalb, IL 60115-2854, USA.

The hydrogen storage properties of the mechanically milled powders were evaluated using an automatic Sieverts apparatus. X-Ray powder diffraction under hydrogen pressure was carried out on a Philips X'pert system using Cu Ka radiation with an Anton Paar XRK9000 pressurized sample holder. Prior to measurement, the sample holder was pumped and flushed with hydrogen three times before establishing a 0.1-MPa hydrogen pressure. The temperature of the already hydrided sample was then increased from 323 to 623 K in 100 K steps and X-ray powder diffraction spectra were acquired at each step. At 623 K, the sample was completely dehydrided. It was rehydrided by reducing the temperature down to 323 K in 100 K steps. To prevent powder movement during the dehydrogenation/ hydrogenation cycle, a beryllium foil of 0.1 mm thickness was put on the sample. The X-ray diffraction patterns were analyzed by the Rietveld method using FULLPROF software [8]. Diffraction lines due to beryllium film and magnesium oxide were removed for this analysis. Lattice parameters, phase abundance, crystallite size and strain were extracted from the Rietveld refinement output.

For synchrotron measurements, the milled powder was cold pressed under a pressure of 2 GPa for 2 min to form a 1-mm-thick pellet. Synchrotron X-ray scattering measurements were carried out at the Advanced Photon Source on the MIT-McGill-IBM beamline using a spectrometer optimized for time-resolved X-ray diffraction [9]. A diamond crystal monochromator was used to produce 7.66-keV X-rays having a relative bandwidth  $\Delta \lambda / \lambda = 6.2 \times 10^{-5}$  and a flux of  $\sim 5 \times 10^{12}$  photons per s for a storage ring current of 100 mA. A linear photodiode array detector (PSD) collected the scattered X-rays. The detector was placed 75 mm from the sample, covering a  $2\theta$  range of about  $20^{\circ}$ , and scattering patterns could be acquired as fast as every 5 ms. Samples were placed inside a vacuum furnace with a Be window giving access to about  $200^{\circ}$  in  $2\theta$ . Prior to heating the sample, the furnace was flushed with nitrogen and pumped down to a pressure of  $\sim 1 \times 10^{-6}$  Torr. The sample was then heated until dehydrogenation occurred and X-ray patterns were continuously acquired during that process.

## 3. Results and discussion

## 3.1. Hydrogen sorption kinetics

Hydrogenation kinetics at various temperatures of the nanocomposite  $MgH_2$ -Nb5at.% are presented in Fig. 1. For comparison, the hydrogenation curve at 573 K of the nanocomposite  $MgH_2$ -V5at.% is also shown. From these curves it can be seen that, except for a smaller hydrogen capacity, the hydrogenation kinetics in  $MgH_2$ -Nb nanocomposite is as fast as in the  $MgH_2$ -V system. The smaller capacity is easily explained by the fact that 5at.% translates to 9wt.% for vanadium and 15wt.% for niobium

Fig. 1. Hydrogenation kinetics of  $MgH_2$ -Nb5at.% and  $MgH_2$ -V5at.% nanocomposites at various temperatures under a hydrogen pressure of 1.0 MPa.

nanocomposites. The curves for  $MgH_2-Nb$  and  $MgH_2-V$ nanocomposites also have the same shape, suggesting that they have the same hydrogenation rate-limiting step. Dehydrogenation kinetics of  $MgH_2-Nb$  and  $MgH_2-V$ nanocomposites are shown in Fig. 2. As for hydrogenation, identical shapes indicate that  $MgH_2-Nb$  and  $MgH_2-V$ nanocomposites have the same rate-limiting steps. A study of rate-limiting step and activation energy in  $MgH_2-V$ system has been reported by Liang et al. [5]. It was found that for temperatures above 523 K and low hydrogen pressure, dehydrogenation is interface controlled, two-di-

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Fig. 2. Dehydrogenation kinetics of  $MgH_2-Nb5at.\%$  and  $MgH_2-V5at.\%$  nanocomposites at various temperatures under a hydrogen pressure of 0.015 MPa.



mension growth. At temperatures between 473 and 523 K, the rate-limiting step of dehydrogenation is nucleation with a two-dimensional growth.

### 3.2. Structure

In order to understand the structural changes due to hydrogenation/dehydrogenation, X-ray powder diffraction was performed in-situ under a hydrogen pressure of 0.1 MPa. The collected patterns are shown in Fig. 3 and their evolution was discussed in Ref. [7]. In these patterns, the niobium hydride peaks are strong and easy to recognize, contrary to the case of vanadium peaks in MgH<sub>2</sub>-V5at.%. This is the main reason why the nanocomposite MgH<sub>2</sub>-Nb5at.% was used for structural studies. A Rietveld refinement was performed on each pattern and the lattice parameters and crystallite size were extracted from each fit. The lattice parameters of  $\beta$ -MgH<sub>2</sub>,  $\beta$ -NbH and Mg are, respectively, shown in Figs. 4, 5 and 6. For the  $\beta$ -MgH<sub>2</sub> phase, the lattice parameters slightly increase with temperature. There seems to be a discontinuity in the c lattice parameter at 623 K. However, at this temperature the abundance of  $\beta$ -MgH<sub>2</sub> phase is only 2wt.%, and this induces a large uncertainty in the determination of the lattice parameters. For the NbH phase prior to dehydrogenation (323 K), the a and b lattice parameters are quite close to values found in the literature. On the other hand, the c lattice parameter is much smaller than the published value. This may be as a result of constraints imposed by MgH<sub>2</sub> and/or internal strain. When the sample is heated from 423 to 623 K, the c lattice parameter slowly increases. However, even when the temperature is reduced



Fig. 3. X-Ray powder diffraction pattern under 0.1 MPa of hydrogen of ball milled  $MgH_2$ -Nb5at.% nanocomposite during dehydrogenation/re-hydrogenation cycle. The time sequence of X-ray patterns is from bottom to the top of the graph. Part of the patterns where strong diffraction lines from sample holder are present is removed.

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Fig. 4. Lattice parameters of  $\beta$ -MgH<sub>2</sub> phase during the dehydrogenation/ rehydrogenation cycle. Maximum error bars are indicated on one set of data points. As a reference, the literature values are indicated by filled symbols on the right-hand axis of the graph.

from 623 to 523 K, the *c* parameter continues to grow until it reaches the literature value. This fact indicates that the changes in lattice parameters of the NbH phase are due to the hydrogenation/dehydrogenation of the magnesium and not to the change in temperature. In Fig. 6, the lattice parameters of nanocrystalline magnesium are shown. The *a* lattice parameter is identical to the polycrystalline case while for the *c* parameter, the slope is about the same but with values slightly higher. It is known that, compared to polycrystalline materials, the thermal expansion coefficient of nanocrystalline materials is usually higher [10]. However, it is not the case for this system. This suggests that the thermal expansion of the grain boundaries is similar to the crystalline contribution in nanocrystalline magnesium.



Fig. 5. Lattice parameters of  $\beta$ -NbH phase during the dehydrogenation/ rehydrogenation cycle. Maximum error bars are indicated on one set of data points. As a reference, the literature values are indicated by filled symbols on the right-hand axis of the graph.



Fig. 6. Lattice parameters of Mg phase during the dehydrogenation/ rehydrogenation cycle. Representative error bars are indicated on one set of data points. The dashed curves show the calculated values for polycrystalline magnesium [18].

## 3.3. Crystallite size

From the peak width parameters given by Rietveld refinement of the diffraction patterns of Fig. 3, the crystallite size evolution during a hydrogenation/dehydrogenation cycle was investigated. Results are shown in Fig. 7. It could be observed that upon cycling,  $\beta$ -NbH crystallites slightly increase from  $30\pm3$  to  $56\pm5$  nm. The largest variation is observed for magnesium. At the beginning of the cycle, magnesium is fully hydrogenated and  $\beta$ -MgH<sub>2</sub> has a crystallite size of 8.3±0.3 nm. As the temperature increases, the crystallites size increases only marginally and reaches 12.5±0.3 nm at 523 K. At 623 K most of the magnesium is in a desorbed state. Only 2wt.% of  $\beta$ -MgH<sub>2</sub> remains and the crystallite size of this phase is  $45\pm2$  nm. On the other hand, magnesium abundance is 80wt.% (the remaining part is  $\beta$ -NbH at 18wt.%) and its crystallite size is much larger at 740±110 nm. Therefore,



Fig. 7. Crystallite size of  $\beta$ -MgH<sub>2</sub>,  $\beta$ -NbH and Mg phases during the dehydrogenation/rehydrogenation cycle.

magnesium experiences an increase in its coherence length when it changes from a hydrogenated to a dehydrogenated state. When the temperature is reduced and the sample is re-hydrogenated, the crystallite size of  $\beta$ -MgH<sub>2</sub> stabilizes at 236±20 nm (phase abundance 75wt.%), a value still smaller than the magnesium crystallite size at the onset of the first dehydrogenation. At 323 K, only a small part of magnesium did not rehydrogenate and stayed in magnesium phase (9wt.%) with a crystallite size of 39±6 nm.

#### 3.4. Synchrotron measurement

Fig. 8 shows a typical time-resolved X-ray spectrum and temperature profile of a  $MgH_2$ –Nb nanocomposite sample as it is being heated through dehydrogenation. In this figure, a gray-scale contour plot represents the scattering intensity. The different peaks corresponding to the start and end products are identified on the right-hand side of the figure. The most remarkable feature of this figure is the transformation of niobium hydride into a metastable phase before ultimately converting to Nb. This metastable phase has a composition estimated to be NbH<sub>0.6</sub> and its structure is closely related to a low temperature phase of composition Nb<sub>4</sub>H<sub>3</sub> [6]. In this phase, an ordered structure of H vacancies is formed in the hydrogen sublattice of the  $\beta$  phase [11]. This ordering of empty sites forms channels



Fig. 8. Time-resolved X-ray scattering (wavelength 1.619 Å) of  $MgH_2$ + 5at.%Nb nanocomposite during the dehydrogenation process. (a) Raw data X-ray scattering where lighter tones indicate higher intensities. (b) Temperature profile. Peak labels are on the right-hand side.

through which hydrogen from the main  $MgH_2$  phase can diffuse before being released from the nanocomposite. It was therefore demonstrated that hydrogen coming out of magnesium hydride flows through niobium to exit the material [6]. The interfaces Mg–Nb, formed during ball milling are free of oxygen and therefore are more permeable to hydrogen than an oxidized surface. Furthermore, a certain degree of coherency probably exists between magnesium and niobium lattices at the interface. A similar gateway model was proposed for the catalytic role of Mg<sub>2</sub>Cu in the eutectic alloy Mg/Mg<sub>2</sub>Cu [12,13].

### 3.5. Activation energies

In order to determine the activation energies of the different processes, time-resolved X-ray scattering measurements were obtained at different temperatures. The time evolution of magnesium and niobium phases, as determined by a decomposition of the diffraction pattern into the diffraction pattern of each phase, at temperatures of 543, 563 and 593 K is shown in Fig. 9. This figure clearly indicates that the temporal evolution of the relative abundance of the different phases is identical throughout this temperature range. Upon heating, the signal from  $\beta$ -MgH<sub>2</sub> phase increases due to the transformation of the metastable  $\gamma$ -MgH<sub>2</sub> phase (synthesized by ball milling) into  $\beta$ -MgH<sub>2</sub> [6,14]. When magnesium hydride starts to desorb, niobium hydride (\beta-NbH) also starts to decay at approximately the same rate. Simultaneously, metallic magnesium and the niobium hydride metastable phase appear and grow at the same rate. Finally, when magnesium is fully dehydrogenated, the niobium hydride metastable phase starts to transform into niobium.

For each process, the activation energies were estimated by plotting the maximum rate of change of intensity of each Bragg peak (*k*) as a function of temperature (*T*) in an Arrhenius plot. The activation energies shown in Table 1 were extracted by performing a linear regression of the ln *k* versus 1/T curve. From this table, we see that the activation energy of  $\beta$ -MgH<sub>2</sub> decomposition and magnesium formation agree with each other as it should. It also agrees with the activation energy of dehydrogenation of MgH<sub>2</sub>–V5at.% system reported as 52 kJ/mol [5]. As seen in Figs. 1 and 2, MgH<sub>2</sub>–Nb5at.% and MgH<sub>2</sub>–V5at.% systems have the same hydrogen sorption behavior so they must have the same activation energies.

The activation energy of  $\beta$ -MgH<sub>2</sub> decomposition for conventional polycrystalline material was reported to be in the range from 120 to 142 kJ/mol [13,15,16] while for ball milled magnesium hydride, the value is 120 kJ/mol [14]. The activation energy of  $\beta$ -MgH<sub>2</sub> decomposition in MgH<sub>2</sub>–Nb5at.% (62 kJ mol<sup>-1</sup>) is identical to the activation energy for the formation of the metastable NbH phase (62 kJ mol<sup>-1</sup>). This is higher than the activation energy of diffusion in niobium (10.2 kJ mol<sup>-1</sup>) [11] and magnesium (40 kJ mol<sup>-1</sup>) [17].

Fig. 9. Temporal evolution of the various hydrides and metallic phases of magnesium and niobium for different dehydrogenation temperatures: (a) 593 K, (b) 563 K, (c) 543 K.

Table 1

Activation energies determined from linear fitting of  $\ln k$  versus 1/T plot

Reaction	Activation energy (kJ/mol)
β-MgH <sub>2</sub> decomposition	62(8)
Mg formation	59(9)
β-NbH decomposition	≈77
Metastable formation	62(6)
Metastable decomposition	74(30)
Nb formation	75(45)

Values in parentheses are 1 S.D. For  $\beta$ -NbH decomposition, one data point had to be rejected and the quoted value should be considered as an order of magnitude only.



The activation energies of metastable decomposition and niobium formation have larger uncertainties but they agree with each other and are quite close to the more precise value of the metastable formation. In the case of  $\beta$ -NbH decomposition, a close inspection of the intensity curve shows a shape quite dissimilar from the other curves. The exact reason for this behavior is not known but it had the effect of giving an unreliable inflection point. Therefore, this particular data point had to be rejected and the activation energy value of  $\beta$ -NbH decomposition should be considered as an order of magnitude only.

## 4. Conclusion

In this study, first we confirmed that the nanocomposites MgH<sub>2</sub>-V and MgH<sub>2</sub>-Nb have similar hydrogen sorption properties. A systematic structural study of the nanocomposite MgH2-Nb5at.% was performed. From insitu X-ray powder diffraction, it was found that the change in lattice parameters in NbH phase is induced by the hydrogenation/dehydrogenation of magnesium. It was also found that for this system, the thermal expansion of nanocrystalline magnesium is similar to polycrystalline magnesium. Activation energies were determined from analysis of real-time synchrotron X-ray powder diffraction at different dehydrogenation temperatures. The activation energies found for the different processes indicate that the presence of a metastable niobium hydride phase decreases the energy barrier of magnesium dehydrogenation. This tends to confirm the gateway model proposed for dehydrogenation in Mg-Nb nanocomposite. Since the kinetics of MgH<sub>2</sub>-V and MgH<sub>2</sub>-Nb are identical, it appears that diffusion through magnesium is the limiting process during dehydrogenation.

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