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In-situ neutron diffraction investigation of Mg_2FeH_6 dehydrogenation

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ABSTRACT

In this paper we present an in-situ neutron diffraction experiment on the dehydrogenation of Mg_2FeH_6 . Stoichiometric mixtures of $2\text{Mg} + \text{Fe}$ were ball milled in a hydrogen environment. After desorption, the samples were exposed to different combinations of hydrogen/deuterium at different temperatures in order to absorb hydrogen or deuterium at specific synthesis steps. Using this hydrogen/deuterium absorption mixture, we found that there may be a hydrogen–deuterium exchange happening when both Mg_2FeH_6 and MgD_2 are present.

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Introduction

As can be seen on the Mg–Fe phase diagram, Magnesium and Iron are immiscible and do not alloy [1]. However, as predicted by Miedema's law of reverse stability, the ternary hydride Mg_2FeH_6 should be stable [2,3]. In fact, Mg_2FeH_6 is part of a family of hydrides of the general form $\text{M}_m^{\delta+}[\text{TH}_n]^{\delta-}$, where M is an alkaline, alkaline earth or a divalent rare earth metal and T is a transition metal [4]. Formation of complex Mg hydrides has been studied by Deledda and Hauback [5] and by Baum et al. [6]. In the case of Mg_2FeH_6 , the building block is the octahedral anion complex $[\text{FeH}_6]^{4-}$ [7]. Compared to magnesium hydride, Mg_2FeH_6 has a slightly lower hydrogen gravimetric capacity (5.4 wt.% versus 7.6 wt.%), but a higher volumetric capacity (9.1×10^{22} atoms/cm³ versus 6.5×10^{22}

atoms/cm³). The reported heat of formation for Mg_2FeH_6 is disputed. Values of -98 ± 3 kJ/mol [7], -86 ± 6 kJ/mol [8] and -81 ± 28 kJ/mol [9] have been proposed. Nevertheless, these are all lower than $\beta\text{-MgH}_2$'s heat of formation (-75 kJ/mol) which means that Mg_2FeH_6 is more stable than $\beta\text{-MgH}_2$. These properties have created interest in Mg_2FeH_6 for both hydrogen and heat storage applications [10].

In a previous investigation using Electron Energy-Loss Spectroscopy (EELS) and electron microscopy, we saw that when a ball milled stoichiometric mixture of $2\text{Mg} + \text{Fe}$ was exposed to a hydrogen pressure of 40 bar at 673 K, the ternary hydride phase Mg_2FeH_6 was formed. It grew with a columnar morphology emerging from Fe capped MgH_2 particles [11]. From EELS measurements, a shift in the plasmon frequency of Mg_2FeH_6 was found. This shift was tentatively attributed to either a slight rearrangement of the hydrogen atoms or a

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modification of the crystal structure leading to a metastable phase. In this paper, we will show that iron particles act as a catalyst to generate atomic hydrogen and also as one of the reactants to form Mg_2FeH_6 .

Since Mg_2FeH_6 is more stable than MgH_2 , in principle, it should be the first to form during hydrogenation. However, formation of the ternary hydride implies the interdiffusion of Mg and Fe, which makes the hydride formation kinetically limited. Therefore, under most conditions, the preferred reaction pathway is a two-step mechanism where MgH_2 plays the role of Mg_2FeH_6 precursor [12–16]. However, if at a given temperature, the applied hydrogen pressure is below the equilibrium pressure of MgH_2 but above the one for Mg_2FeH_6 , then the ternary hydride will be directly synthesized [17].

In order to gather more information on the hydrogenation and dehydrogenation behavior of this system, we performed in-situ neutron diffraction on a family of samples that underwent different hydride formation paths. Some were exposed to hydrogen, some to deuterium and others to a sequence of hydrogen and deuterium. In this way, the hydrogenation pathway could be investigated.

Materials and methods

In this study, we used Mg (–300 mesh, 99.8% purity), Fe (–22 mesh, 98% purity) and MgH_2 (–300 mesh, 96% purity), all in powder form and bought from Alfa Aesar. Samples were prepared by ball milling stoichiometric mixtures of Mg–Fe using a pulverisette 4 in a 218 cc stainless steel crucible containing 20 stainless steel balls of 10 mm in diameter, with a ball-to-powder weight ratio of 40:1. The $2\text{Mg} + \text{Fe}$ stoichiometric mixtures were ball milled for 12 h under 3 MPa of hydrogen. After milling, the samples were dehydrogenated at 623 K under vacuum. The samples were then exposed to different gases (Hydrogen or Deuterium) at different pressures and temperatures. Table 1 shows each sample's preparation specifications.

The $2\text{MgD}_2 + \text{Fe}$ sample was synthesized under conditions where only the MgH_2 phase would be produced. In a similar way, during the Mg_2FeD_6 synthesis, conditions were selected so that only this phase would be synthesized. The samples $\text{Mg}_2\text{Fe}(\text{H},\text{D})_6$ and $\text{Mg}_2\text{Fe}(\text{D},\text{H})_6$ were synthesized under conditions where the first reaction would produce MgH_2 or MgD_2 in the first step. The second step was favorable to the synthesis of Mg_2FeD_6 or Mg_2FeH_6 . Using different absorption gases allowed us to probe the interaction between the MgH_2 and Mg_2FeH_6 phases. All samples were quenched at room temperature after synthesis.

Neutron powder diffraction was carried out by the Neutron Scattering Branch (NSB) at the Canadian Nuclear Laboratories'

Table 1 – Sample composition and absorption details.

Sample composition	Sample absorption details
$2\text{MgD}_2 + \text{Fe}$	573 K/10 bar D_2
Mg_2FeD_6	673 K/17 bar D_2
$\text{Mg}_2\text{Fe}(\text{H},\text{D})_6$	573 K/10 bar $\text{H}_2 + 673 \text{ K}/25 \text{ bar } \text{D}_2$
$\text{Mg}_2\text{Fe}(\text{D},\text{H})_6$	573 K/10 bar $\text{D}_2 + 673 \text{ K}/25 \text{ bar } \text{H}_2$

(CNL) NRU reactor in Chalk River, Ontario. Using the C2 800 wire neutron detector and a homemade gas delivery apparatus for in-situ studies. Using an Argon glovebox, the as-received powder was loaded into a Copper coated Vanadium sample holder. The sample holder has a volume of 4.75 cc and is equipped with a VCR fitting that connects to the gas delivery apparatus via a ¼ inch stainless steel VCR component. The sample holder's wall thickness is approximately 1 mm and the copper coating is roughly 2 microns thick. The sample holder was placed in a high-vacuum aluminum chamber where it is surrounded by a Tantalum heater. A vacuum was pulled in the gas delivery system and then, the sample stick's manual valve was opened. This procedure keeps the sample under vacuum, making sure it is not exposed to air.

As a baseline, each sample was first measured under vacuum at room temperature. After the baseline pattern, the temperature set point was raised from 293 K to 523 K and the temperature control ramp was set to 2 K/min.

Diffraction patterns were constantly recorded as the temperature rose, allowing us to “follow” the reaction using neutron powder diffraction. The detector spans from 5 to 85° 2 θ which means that the detector needs to be moved to a high angle position to record a full 0–120° pattern. During this study, we opted not to move the detector, thus allowing us to effectively double the number of recorded patterns during each reaction. Diffraction patterns were also recorded after a full desorption before cooling the sample back to room temperature, where a final neutron diffraction pattern was recorded.

The patterns were then analyzed by Rietveld refinement, using Bruker's TOPAS 5.1 software. The crystallographic parameters used in our Rietveld refinements were taken from Konstanchuk et al. for Mg_2FeH_6 phase [8] and from Ellinger et al. for the MgH_2 phase [18]. The parameters are presented in Table 2.

Results

As all results will be quoted in wt.%, we should mention that the nominal abundance of Mg and Fe in all samples are respectively 46 and 54 wt.%. Rietveld refinement analysis has,

Table 2 – Crystallographic information of the hydride/deuteride phases used in Rietveld refinements. Parameters for the MgH_2 phase are from Ref. [6] and parameters for Mg_2FeH_6 are from Ref. [16].

Phase	Mg_2FeH_6		
Space group	$Fm\text{-}3m$ (225)		
Lattice parameters	$a = b = c = 6.442 \text{ \AA}$		
Atomic coordinates	Element	Wyckoff	Position (x, y, z)
	H	24e	0.23723, 0, 0
	Mg	8c	¼, ¼, ¼
	Fe	4a	0, 0, 0
Phase	MgH_2		
Space group	$P4_2/mnm$ (136)		
Lattice parameters	$a = b = 4.5168, c = 3.0205 \text{ \AA}$		
Atomic coordinates	Element	Wyckoff	Position (x, y, z)
	H	4f	0.306, 0.306, 0
	Mg	2a	0, 0, 0

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