

Structural analysis of activated $\text{Mg}(\text{Nb})\text{H}_2$

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Abstract

A metastable niobium hydride, believed to trigger rapid H desorption from the MgH_2 matrix, was detected in the course of real time synchrotron diffraction studies of the desorption kinetics of hydrogen in MgH_2 with about 5% NbH nanoparticles. In order to completely characterize this metastable phase, we performed in situ neutron diffraction experiments during hydrogenation/dehydrogenation of a magnesium–niobium nanocomposite. At 250 °C (under 1 bar of H pressure) a hydride phase NbH_x appears. Unfortunately, the available low pressure together with the low q -range did not allow to propose a structural arrangement for this phase. We thus switched to standard neutron diffraction (that is at constant pressure and room temperature) of ball-milled Mg–Nb–H nanocomposites for which various NbH hydrides were detected including the solid solution. It turns out that the formation of these niobium hydrides (metastable or not) is closely related to the milling time and depends on the quality of the starting metal.

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1. Introduction

Because magnesium hydride (MgH_2) has a high hydrogen storage capacity (7.6 wt.%), it could be considered as an attractive material for energy storage. However, due to the hydride stability and slow sorption kinetics, the actual applications are limited. It has been shown that the ball-milled nanocomposite MgH_2 –V possess fast hydrogen sorption kinetics and could absorb hydrogen even at room temperature [1]. However, the exact role of the additive and the mechanism by which hydrogen flows in and out of the hydride was still unclear. In order to have a better understanding of this mechanism, a systematic study of structural changes in the nanocomposite MgH_2 –5 at.% Nb was performed using X-ray diffraction under hydrogen pressure

and in situ time-resolved X-ray scattering of synchrotron radiation. For these studies, MgH_2 –5 at.% Nb nanocomposite was selected because niobium is a better X-ray scatterer than vanadium, and MgH_2 –5 at.% Nb nanocomposite has similar sorption properties than MgH_2 + 5 at.% V [2] with non-overlapping X-ray peaks [3]. From in situ time-resolved X-ray scattering of synchrotron radiation it was found that hydrogen desorption involves the formation of a short-lived metastable niobium-hydride phase which acts as a gateway through which hydrogen released from MgH_2 is flowing [4].

In order to completely characterize this metastable phase, we report in this paper on in situ neutron diffraction experiments during hydrogenation/dehydrogenation of a similar magnesium–niobium nanocomposite. In addition to these experiments, a series of neutron diffraction patterns was recorded on ball-milled Mg–Nb–H nanocomposites at various milling times.

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2. Experimental details

2.1. Samples synthesis

Details about the sample preparation of the MgH₂–5 at.% Nb nanocomposite used for in situ experiments can be found in reference [5]. The other set of samples was elaborated as follows: batches of commercial Mg powders (Metal Composites Powders Technologies SA, grain sizes below 40 μm) were deuterated in laboratory-made autoclaves under 20 bars at 350 °C. These MgD₂ powders were then mixed with 5 at.% niobium. Hardened steel crucibles of 3 cm diameter containing three hard steel balls of 8.5 g weight each were charged with powders and locked under argon. The balls to powder weight ratio was 10:1. The planetary machine (Fritsch Pulverisette 5) was used at a rotation speed of 360 rpm and with a large range of different milling times: 15 min, 1, 5, 20 and 60 h, respectively.

2.2. Neutron diffraction

The deuterium desorption/absorption in nanocomposite Mg–Nb was followed in situ using the D20 diffractometer at ILL which was operated at a wavelength of 2.415 Å and using a dedicated high-pressure cell. We encountered some problems in maintaining a leak-free environment at high pressures. However, we were able to perform few desorption processes under vacuum and also a few absorption under deuterium pressure. Unfortunately we were limited to low pressures due to the cell design and for the first experiments we aimed to evaluate the reactivity of the systems in order to prevent any excessive risks.

The neutron diffraction patterns of ball-milled samples at various milling times were collected on the PUS diffractometer at IFE Kjeller and on the D2b diffractometer at ILL both operated at the wavelength of 1.594 Å.

3. Results and discussion

3.1. In situ experiment

In Fig. 1, we present the deuterium absorption under 1 bar at 250 °C. The acquisition time for each pattern was 30 s due to the high flux available. Before the pressurization with deuterium gas, the diffraction pattern shows only magnesium, magnesium oxide and niobium metal phases. After only 4 min under a deuterium pressure of 1 bar, the diffraction pattern shows the appearance of a new phase Nb–H while at the same time there was no sign of the formation of magnesium deuteride. We attempted to fit this Nb–H phase by Rietveld refinement using NbD_{0.89} as a starting model, but the fit was rather limited due to the low q -range on one hand, and also due to the fact that we are dealing with a dilute phase (there is only a few at.% of Nb). However, a series of attempts in the pattern matching mode indicate that this Nb–H phase may

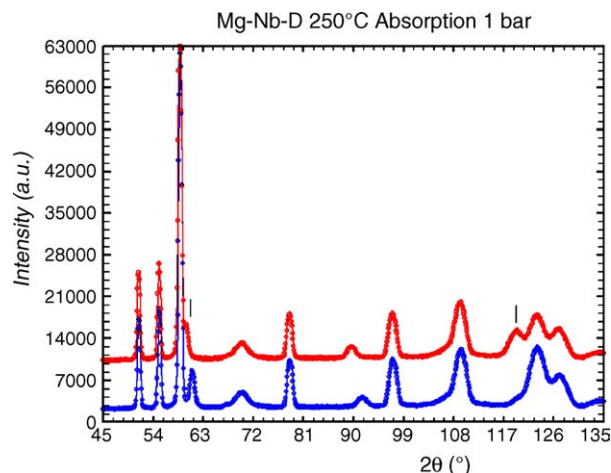


Fig. 1. Mg–Nb deuterium absorption at 250 °C, 1 bar D₂. The upper diffraction pattern shows the formation of the NbD phase (marker lines). Elapsed time between lower and upper pattern is 30 s.

be related to the metastable phase previously identified by synchrotron measurements.

It appears clear that after only the the NbD_{0.89} phase was formed, the MgD₂ phase starts to form as seen on the 3D plot of Fig. 2; but formation of this later hydride remained very limited due to the rather low applied pressure. Moreover from this plot, it appears that the transformation Nb to NbD is a first order-type transition.

Three positive teachings may be drawn from this experiment:

- formation of a Nb–H phase as a precursor;
- this formation seems to anticipate that of MgD₂ (tetragonal rutile type) itself, thus corroborating the sequence that was detected in the course of in situ synchrotron experiments;
- the process appears to be fully reversible when desorbing at high temperatures.

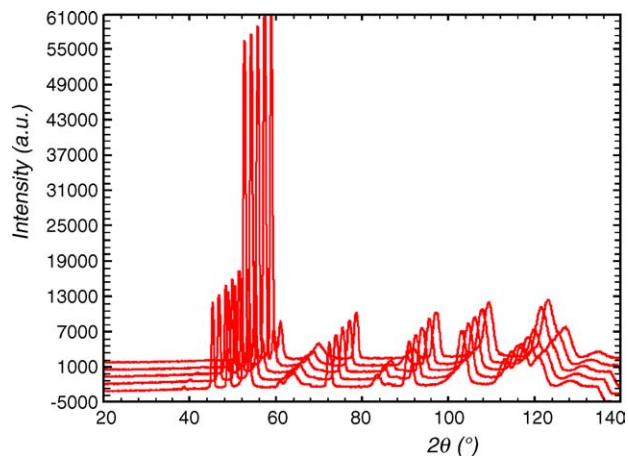


Fig. 2. 3D plot of the: Mg–Nb deuterium absorption at 250 °C, 1 bar D₂.

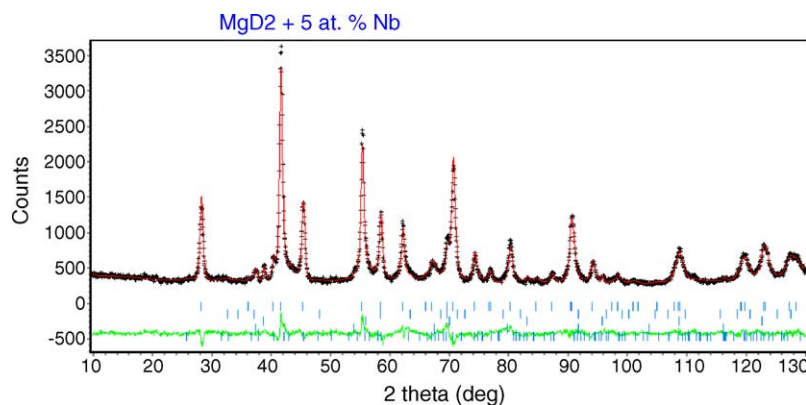


Fig. 3. Rietveld refinement of $\text{MgD}_2 + 5\% \text{ Nb}$ (5 h milled alloy). From top to bottom, reflection markers indicate MgD_2 (tetragonal form), Mg, Nb, NbD_2 , and MgD_2 (meta stable orthorhombic form).

3.2. Neutron diffraction on ball-milled samples

We thereafter report on the results obtained at IFE Kjeller.

$\text{MgD}_2 + 5\% \text{ Nb}$ (5 h milled alloy)

Five phases could be identified in this sample as can be seen from Fig. 3. The peak centred just under 39° is pure Nb. The peak at 37.5° shows the presence of a small amount of unactivated Mg as the leading edge. An interesting feature was the detection of body centred NbD_x . There are four available tetrahedral D sites on each face in the $Im\bar{3}m$ NbD_x structure, resulting in a total of 12 sites (12d Wykoff position) that can only be partially occupied because of D–D separation requirements. The orthorhombic metastable MgD_2 gamma phase is also present as the very strong trailing edge of the structure that begins just after 42° . The refined D occupancy in the $Im\bar{3}m$ NbD_x structure yields a single D atom in approximately every five unit cells, so the D occupation is only very small, and corresponds to very understoichiometric $\text{NbD}_{0.2}$, so this is at best only a bcc solid solution. Alternative niobium deuterides were carefully tested, namely orthorhombic and cubic (fcc) NbD_x structures, but the

only satisfactory agreement was obtained with the bcc solid solution.

$\text{MgD}_2 + 5\% \text{ Nb}$ (20 h milled alloy)

As can be seen in Fig. 4, it is immediately clear that this 20 h sample is substantially different to the 5 h sample. There is no evidence of pure Nb but bcc NbD_x is still present as a weak asymmetric high angle shoulder on the very strong (1 0 1) pure Mg reflection at 37° . I have fixed the D occupancy in the NbD_x structure here at the refined value from the 5 h sample, as it is impossible to refine the occupancy from a single reflection in a weak shoulder. There is a huge increase in unactivated Mg, with a lot of D loss from tetra MgD_2 . The transient γ - MgD_2 phase is still clearly present. It thus appears that the pure Nb has dispersed in the 20 h sample.

At this stage an additional series of neutron powder diffraction experiments was performed using a high flux diffractometer in order to have better counting statistics. For this doing, a new series of sample batches was synthesized. Neutron diffraction revealed that Mg deuteration was not complete since the main phase present on the diffraction patterns was Mg whatever the milling time. After 5 h milling time metallic niobium was still present, a sluggish fading of

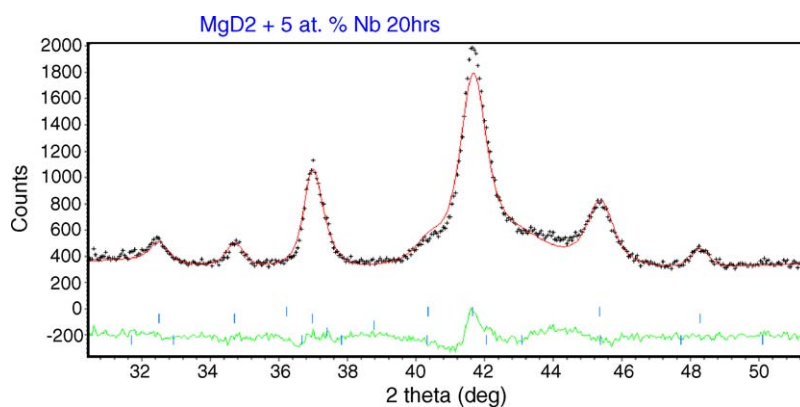


Fig. 4. Detail of the Rietveld refinement of $\text{MgD}_2 + 5\% \text{ Nb}$ (20 h milled alloy).

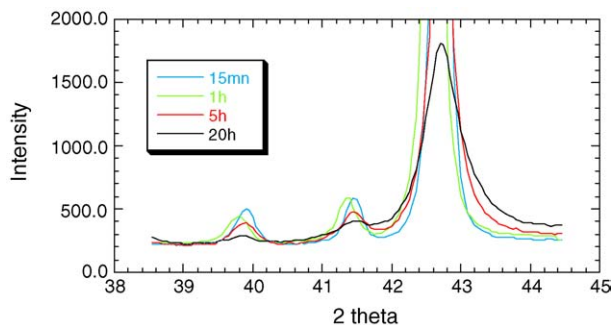


Fig. 5. Fading and/or broadening of the Nb (1 1 0) diffraction line for various milling times.

the Nb (1 1 0) diffraction was merely seen after 20 h milling time (Fig. 5).

4. Conclusion

The series of experiments presented in this paper aims to understand the hydrogen desorption/absorption mechanisms in MgH_2 -Nb nanocomposites. It is now clear that the sequence proceeds in two reversible steps: formation (or de-

composition in the other way) of a Nb-H phase, followed by formation of tetragonal (rutile type) MgH_2 . Two types of niobium hydrides [5,6] have been detected, namely a phase strongly related to the β -NbH (ϵ -phase ?) and a bcc solid solution (α -phase). A correct hydrogen location in the Nb-H phase has still to be solved. In the light of the current experimental data we are not able to decide if the large increase in unactivated Mg is due either to not deuterating the sample for long enough, or whether the problem really is genuinely related to milling time.

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