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Catalytic effects of pseudo AB₂ phases on hydrogen sorption

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Abstract

The compound GdNi₄Mg in its amorphous and crystalline state has been investigated as catalyst for hydrogen sorption of magnesium. Addition of only 0.3 at.% of catalyst by ball milling resulted in an important improvement of hydrogen sorption kinetics. Optimum milling time has been found to be 5 h. The amorphous and crystalline GdNi₄Mg compounds give almost identical kinetics. Both absorption and desorption have been improved and the kinetics obtained are almost the same as other metal catalysts. No evidences of decomposition during ball milling or hydrogenation have been found so that it should be concluded that the intermetallic itself acts as a catalyst.

Keywords: Hydrogen sorption; Magnesium; Catalyst; Ternary compounds

1. Introduction

It is now well-known that the accumulation of CO₂ in the atmosphere is the principal cause of global warming. As long as carbon will be present in any form in the fuel used, the accumulation of CO₂ in the atmosphere cannot be stopped. This leaves us with hydrogen as the only choice as it is the only known carbon free combustible material.

However, the “hydrogen economy” will start only if the problems of hydrogen mass production and storage are solved. In the case of storage, the safety problem of pressurized tank and the high cost of liquefaction bring an interest in an alternative solution: alloys forming metal hydrides. In this case, the storage is based on the reversibility of the reaction with hydrogen of certain metal (Mg, V, Pd, . . .) or intermetallic (LaNi₅, TiMn₂, TiFe, Mg₂Ni, . . .). Amongst all the metal or intermetallics, Mg attracts a lot of efforts because of its low density (1.74 g/cc), high hydrogen capacity (7.6 wt.%) and low cost (less than 5€/kg). However, the reaction with hydrogen is very slow (up to few days to hydride bulk magnesium) and takes place at high temperature (i.e. 300 °C). During the last decades, progress in hydrogenation kinetics of magnesium has been realized by ball milling

[1–6] (in order to increase the number of defects) and addition of some catalysts [7–10] (for the dissociation of hydrogen molecule). The best results are obtained with oxides [8,11–13] as a catalyst but the catalytic effect is not fully understood at the present time. Magnesium-based intermetallics that can be hydrided under ambient conditions have been studied but the results reported were never convincing. Recently, some interest has been focussed on ‘pseudo-AB₂’ compounds of general formula RENi₄Mg [14]. In this work, it has been found that GdNi₄Mg absorbs reversibly hydrogen at room temperature but no significant hydrogen absorption was noticed at 300 °C. Despite this lack of reaction at high temperature, it can be of interest to study the potential catalytic effect of this compound on magnesium hydride formation. In this paper, the effects of milling a mixture of magnesium hydride and 0.3 at.% of GdNi₄Mg in its crystalline and amorphous state are reported. Structural and hydrogen sorption properties have been investigated as a function of milling time. The catalytic effect of GdNi₄Mg and its possible origin have been studied.

2. Experimental details

The magnesium hydride powder MgH₂ (95 wt.% MgH₂, 5 wt.% Mg) was purchased from Th. Goldschmidt AG. The compound GdNi₄Mg was prepared by ball milling stoichiometric amount of Gd, Ni, and Mg powders under argon (p≈0.11 MPa) on a Fritsch Pulverisette 5 for 10 h with a disc rotation speed of 200 rpm. All the handlings were carried out in a glove box under purified argon

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to avoid any air contamination. In the following, the compounds obtained after ball milling will be identified as GdNi_4Mg (a) (where “a” stands for amorphous) and the one obtained after subsequent heat treatment under Ar at 650°C for 1 h will be identified as GdNi_4Mg (c) (where “c” stands for crystallized). More details about the synthesis of the intermetallic compounds can be found in Ref. [14].

The MgH_2 powder was mixed with 0.3 at.% (i.e. 5 wt.%) of GdNi_4Mg in a stainless steel container hermetically closed. Samples were prepared by ball milling the different compounds with a high-energy Spex 8000 Mixer/Mill using a stainless steel milling jar and three hardened steel grinding balls (two balls of 11.1 mm diameter and one ball of 15.9 mm diameter) under argon atmosphere. The initial ball-to-powder mass ratio was 10:1. All handlings of samples were performed inside a glove box with a continuously purified argon atmosphere in order to avoid the oxidation of samples.

The crystalline structure of as-milled powders was characterized by X-ray powder diffraction (XRD) using a Rigaku D-max diffractometer with $\text{Cu K}\alpha$ radiation. The diffraction patterns were analyzed by a whole pattern fitting procedure using the program Fullprof [15] in order to determine the lattice parameters, phase abundance, crystallite size, and strain.

The hydrogen sorption kinetics were measured on a HERA volumetric apparatus [16]. Sorption kinetics were measured at 573 K under 1000 kPa of hydrogen pressure for absorption and 12 kPa for desorption. Other characterizations such as Electron Probe Micro Analyzer (EPMA) (CAMECA SX-100 Instrument), particles size analysis (Malvern Mastersizer Hydro 2000S), and Secondary Electron Microscopy SEM (Jeol 840) have been done before and after hydrogen cycling.

3. Results and discussion

3.1. Crystal structure

The X-ray diffraction patterns of the mixtures $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ (a) ball milled for 1 and 5 h are presented in Fig. 1. Due to the amorphous nature of the catalyst and its low content, it is not possible to detect it by X-ray analysis. After 1 h, the mixture is still well crystallized with an average crystallite size for magnesium hydride (determined from Scherrer formula) of more than 20 nm. After 5 h of ball milling, the magnesium hydride crystallite size decreases to about 9 nm. Moreover, it can be seen that the proportion of the $\gamma\text{-MgH}_2$ phase slightly increases. The peaks relative to the magnesium (coming from the commercial MgH_2) are clearly visible after 1 h of milling and almost disappear after 5 h of milling. This could be due to amorphization [17] or to a large reduction of crystallite size.

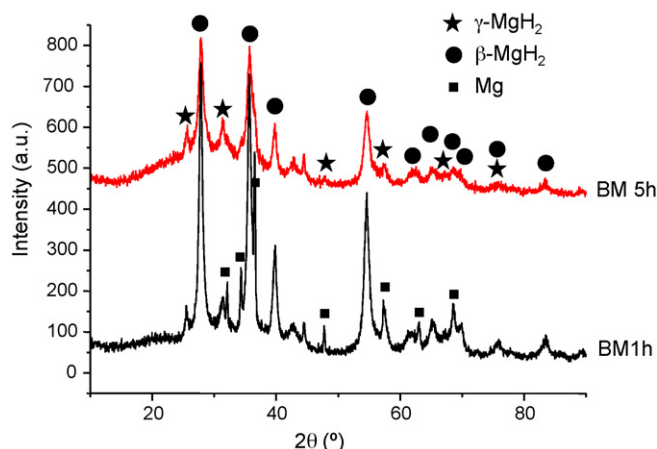


Fig. 1. XRD patterns of $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ (a) ball milled for 1 and 5 h.

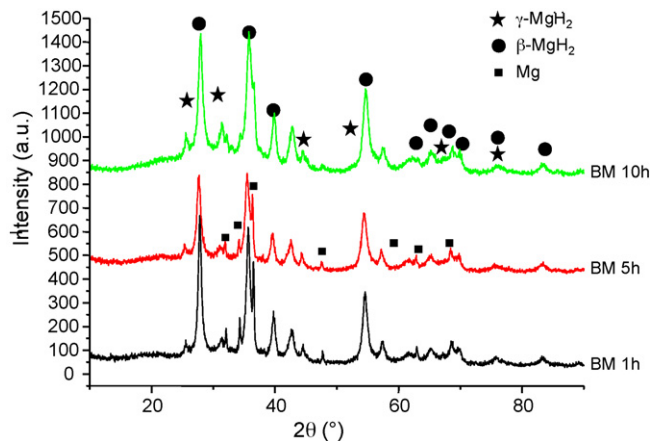


Fig. 2. XRD patterns of $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ (c) ball milled for 1, 5 and 10 h.

Finally, the broad peak around $2\theta = 42^\circ$ is due to MgO , coming from the unreacted Mg present in the commercial MgH_2 .

The X-ray diffraction patterns of the mixtures $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ (c) ball milled for 1, 2 and 5 h are presented in Fig. 2. As the crystallized compound was used, it could be expected to be able to detect it by XRD analysis. However, even before milling (i.e. just manual mixing in a mortar), it was not possible to see the major peak of the GdNi_4Mg (c) (e.g. peak (3 1 1) at $2\theta = 42^\circ$). This result can be explained by the fact that only 0.3 at.% of catalyst was used and that moreover, the catalyst is more dense and the particles size are smaller than MgH_2 . Then, the Mg particles are more present on the surface and as 99% of the X-ray beam is absorbed after $10\ \mu\text{m}$ in Mg , the catalyst cannot be detected. As previously observed with GdNi_4Mg (a), the crystallite size decreases and the relative amount of the $\gamma\text{-MgH}_2$ phase increases with milling time. From 5 to 10 h of milling, the magnesium hydride crystallite size is constant but the relative amount of the γ phase is still increasing. It is also surprising to see that the remaining unreacted magnesium is still present even after 5 h of milling meaning that the crystallite size reduction is less efficient than when the amorphous catalyst is used.

3.2. Hydrogen sorption properties

It could be expected that the structural changes due to milling gives some modification in the hydrogen sorption properties. In the case of the amorphous catalyst, the sorption properties of $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ (a) are presented in Fig. 3a. For the mixtures ball milled for 1 h, the full absorption takes approximately 20 min and desorption is slow (5 wt.% desorbed in 10 min but the full desorption takes about 2 h). When the ball milling is carried on up to 5 h, the sorption properties are greatly improved. The full absorption is reached in about 1 min and desorption is almost complete in 7.5 min. Such results suggest a further increase of milling time but the mixtures ball milled for 10 h (not presented here) exhibit the same properties as the one ball milled for 5 h. Then, it should be concluded that the optimum milling time is close to 5 h.

Fig. 3b represents the result obtained when the crystallized catalyst is used. It is clear from that figure that the effect of ball

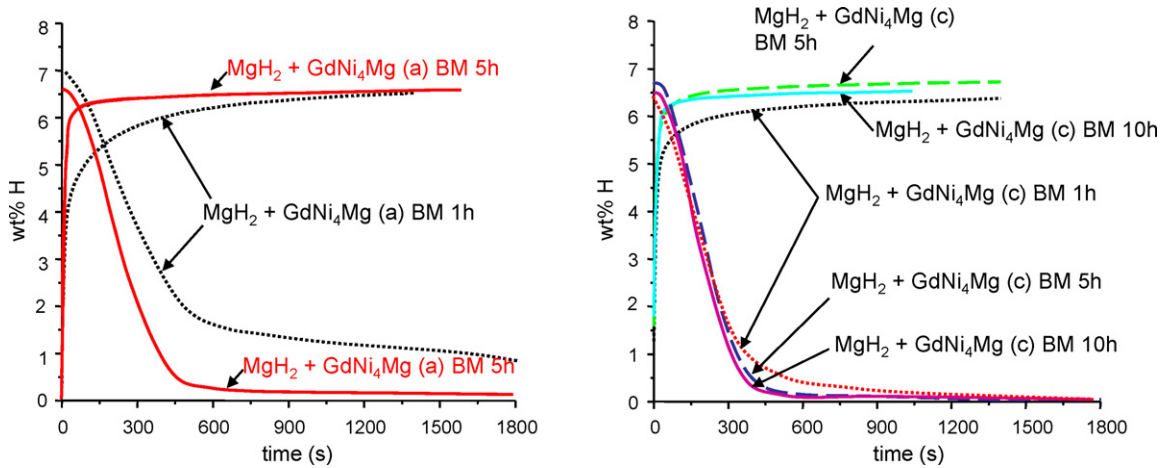


Fig. 3. Sorption kinetics for $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ amorphous (on left) and crystallized (on right) milled for different duration.

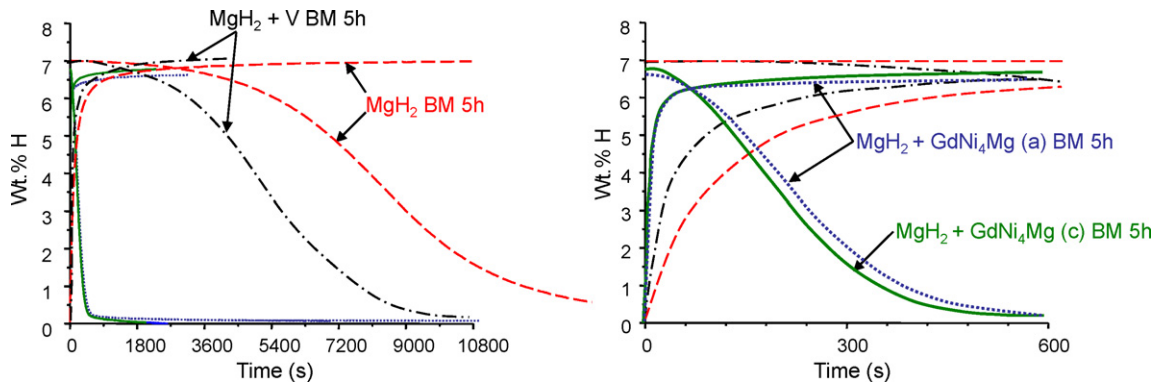


Fig. 4. Comparison between the sorption kinetics of MgH_2 , $\text{MgH}_2 + \text{V}$ and $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ (a) and (c) ball milled for 5 h. The right part is a zoom on the first 10 min.

milling time is very small. The full absorption is reached after 10 min for the mixture milled for 1 h as it is reached in 1 min for the mixture milled for 5 h. The desorption behaves in the same way as after 7 min the mixture ball milled for 5 h is fully desorbed while the mixture ball milled for 1 h desorb only 90% of its hydrogen in the same time. In the same way as for the amorphous catalyst, milling for more than 5 h does not lead to any more increase of the sorption properties.

3.3. Comparison with other catalysts

In order to estimate the catalytic effect of GdNi_4Mg (a) or GdNi_4Mg (c), a comparison with pure MgH_2 and other catalysts is judicious. As the GdNi_4Mg forms a stable hydride under ambient conditions, it is interesting to compare with another catalyst that has similar behavior. In this respect, vanadium is a good choice because it is a well-known catalyst for magnesium and it

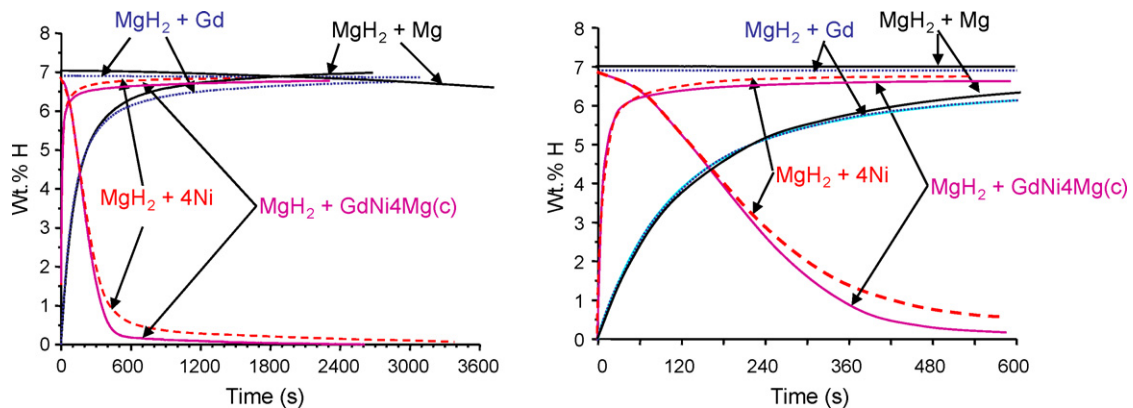


Fig. 5. Comparison between the effects of the “elemental” dopants and “compounds” dopants. All mixtures are ball milled for 5 h.

forms a stable hydride. Thus, a mixture of $\text{MgH}_2 + \text{V}(0.3 \text{ at.}\%)$ was ball milled for 5 h under argon atmosphere in the same conditions as previously. Pure magnesium hydride was also milled for 5 h in argon in order to see the effect of milling on the sorption kinetics. In Fig. 4, the sorption properties of ball milled pure MgH_2 and mixture $\text{MgH}_2 + \text{V}(0.3 \text{ at.}\%)$ compared to ball milled magnesium hydride doped with $\text{GdNi}_4\text{Mg(a)}$ and $\text{GdNi}_4\text{Mg(c)}$ are presented. It shows that complete absorption is reached in 1 min for magnesium hydride doped with $\text{GdNi}_4\text{Mg(a)}$ or $\text{GdNi}_4\text{Mg(c)}$, but it takes more than 10 min for $\text{MgH}_2 + \text{V}(0.3 \text{ at.}\%)$ and pure MgH_2 .

The discrepancy between vanadium and GdNi_4Mg doped magnesium hydride is even more remarkable for the desorption process. The full desorption takes only 7–8 min for the $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ mixtures while it requires 3 h for $\text{MgH}_2 + \text{V}$ and even 5 h for pure MgH_2 . Fig. 4b shows that, for the mixtures milled for an optimum time of 5 h, the difference between the mixtures containing the crystallized or the amorphous compounds is small for both absorption and desorption processes. Only a small difference can be seen on the desorption process where the mixtures with $\text{GdNi}_4\text{Mg(c)}$ shows slightly better kinetics.

In order to get a better understanding of the catalytic effect, mixtures containing the same atomic content of elemental catalysts element than the alloy (i.e. $\text{MgH}_2 + 0.3 \text{ at.}\% \text{ Mg}$, $\text{MgH}_2 + 0.3 \text{ at.}\% \text{ Gd}$ and $\text{MgH}_2 + 1.2 \text{ at.}\% \text{ Ni}$) were ball milled for 5 h under the same conditions. The hydrogen sorption properties are presented in Fig. 5. The mixtures containing Gd or Mg as a catalyst behave almost on the same way. The full absorption is

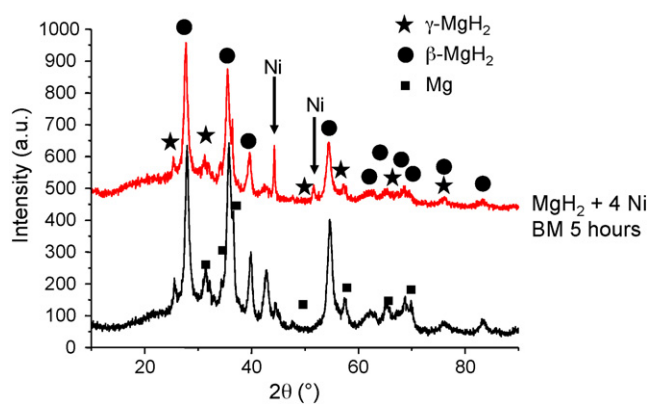


Fig. 6. XRD patterns of $\text{MgH}_2 + 4 \text{ Ni}$ ball milled for 5 h. For a matter of comparison, the XRD of $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ BM in the same conditions is given on the bottom.

reached after 20 min (but 6 wt.% of hydrogen is already reached after 10 min) but desorption is a very slow process. After the first hour, only 0.5 wt.% of hydrogen has been desorbed from the mixtures. The mixture doped with 1.2 at.% Ni behaves in a very similar way to the mixture containing GdNi_4Mg . On absorption, the first minute is strictly comparable and beyond the mixture with 1.2 at.% Ni is slightly better. On the desorption process, the behavior is comparable during the first 3 min and beyond it is the mixture with GdNi_4Mg which is better.

As both 1.2 at.% Ni and 0.3 at.% GdNi_4Mg have the same catalytic effect it is worth checking the structural properties. The XRD patterns of both mixtures are presented in Fig. 6. It is

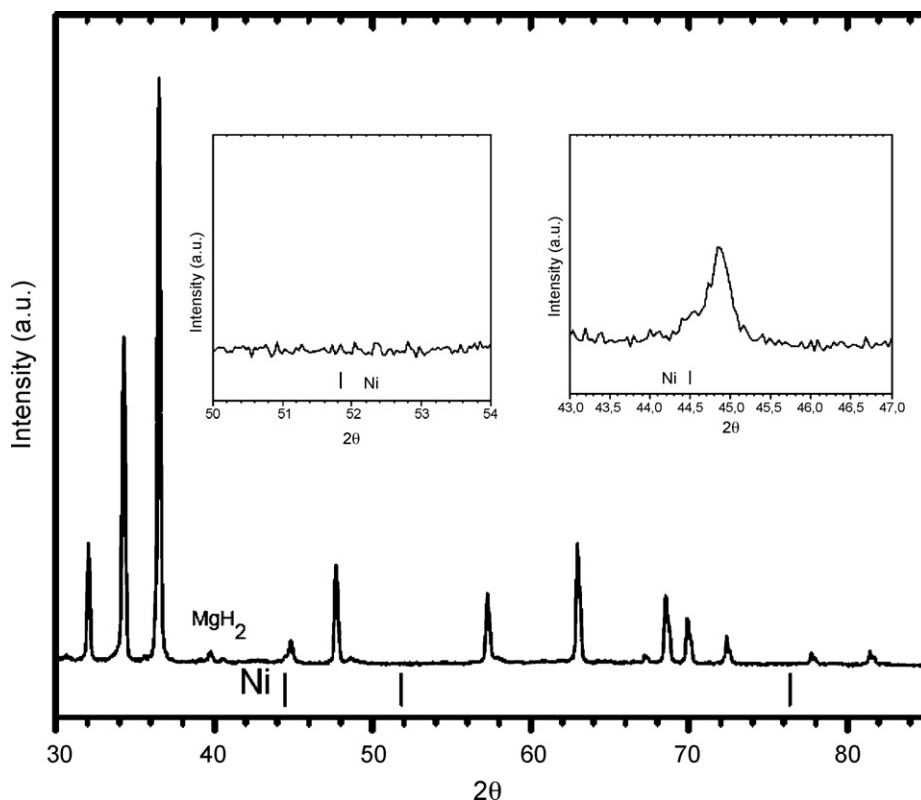


Fig. 7. XRD patterns of $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ BM ball milled for 5 h, after four hydrogenation/dehydrogenation cycle in the dehydrogenated state.

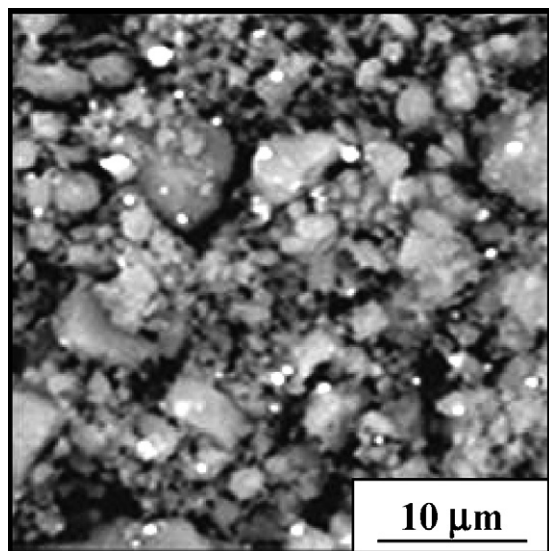


Fig. 8. SEM observation of the $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ (c) ball milled for 5 h.

clear from this figure that in the mixtures $\text{MgH}_2 + 1.2 \text{ at.} \% \text{ Ni}$, nickel stays well crystallized and does not form intermetallic compound with magnesium or magnesium hydride. In the case of $\text{MgH}_2 + 0.3 \text{ at.} \% \text{ GdNi}_4\text{Mg}$ mixture there is no evidence of elemental nickel.

A possible explanation of the similar catalytic effect of $1.2 \text{ at.} \% \text{ Ni}$ and $0.3 \text{ at.} \% \text{ GdNi}_4\text{Mg}$ may be that the GdNi_4Mg compound decomposes during milling or during subsequent hydrogenation. The X-ray powder diffraction of Fig. 6 does not support decomposition due to ball milling. To check the decomposition due to hydrogen cycling, a powder diffraction pattern was taken on a dehydrogenated sample. Fig. 7 is the diffraction pattern of ball milled $\text{MgH}_2 + \text{GdNi}_4\text{Mg}$ (c) cycled 4 times and in a dehydrogenated state. All peaks are indexed to pure magnesium except for a small peak near 40° which is due to hydrided magnesium. Another small peak near 45° is close to the (1 1 1) Bragg peak of pure nickel. However, as shown in the inset, the nickel reflection does not correspond to the main diffraction peak. Moreover, the second inset demonstrate that the (2 0 0) nickel reflection is totally absent. A further test of the decomposition hypothesis have been performed by SEM analysis as well as EPMA. The SEM (backscatter radiation) micrograph shown in Fig. 8 reveals the presence of only 2 phases: one corresponding to the Mg matrix and the other corresponding to the catalyst GdNi_4Mg . The catalyst is well dispersed after 5 h of milling and particle size range from 0.1 to almost $5 \mu\text{m}$. The EPMA investigation revealed a difference between mixtures containing amorphous and crystallized catalysts: After 1 h of milling the amorphous catalyst is not as well dispersed as the crystallized one and some large agglomerates can be observed.

Tests of sorption kinetics at different temperatures for magnesium hydride doped with $1.2 \text{ at.} \% \text{ Ni}$ and $0.3 \text{ at.} \% \text{ GdNi}_4\text{Mg}$ gave identical kinetics for absorption and desorption. Even if the catalytic mechanism for nickel and GdNi_4Mg is the same, the fact that the kinetics of both mixtures are identical should still be explained. One possible explanation, given the fact that the kinetics are very fast, could be that the rate limiting step

is no longer due to the catalyst but is now heat transfer. One advantage of using GdNi_4Mg as catalyst instead of nickel is the fact that upon cycling nickel will form the intermetallic Mg_2Ni while in the case of GdNi_4Mg our preliminary results, for a limited number of cycles, indicates that the compound does not decompose.

Experiments with 50 wt.% of GdNi_4Mg catalyst shows that it is not hydrided during the sorption process which is in agreement with the thermodynamic data of $\text{GdNi}_4\text{Mg-H}$ system. Then, it should be concluded that the catalytic effect of GdNi_4Mg is of the same type as the one of nickel: GdNi_4Mg should act as a catalyst for the decomposition of dihydrogen. It could be of interest to test GdNi_4Mg as a catalyst in some organic reaction where the Raney nickel is usually used in order to definitively validate our hypothesis.

4. Conclusion

Alloys GdNi_4Mg (a and c) that can form a hydride under ambient conditions but do not absorb at high temperature have been used as a catalyst for the sorption of hydrogen in magnesium. To reach the best performances of the mixtures a ball milling time of 5 h is needed. Shorter and longer milling times give slower kinetics. For the optimized milling time mixtures, no significant difference between the mixtures containing the amorphous and the crystallized compounds can be highlighted. The catalytic activity of GdNi_4Mg is comparable to the one of Ni (used in the same atomic proportion) and probably has the same mechanism (i.e. dissociation of molecular hydrogen). These results clearly open some new research approach of new catalyst for both the hydrogen sorption of magnesium but also for the organic chemistry.

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