

# Hydrogen Sorption Properties of the Intermetallic Mg<sub>2</sub>Ni Obtained by Using a Simoloyer Ball Milling

## *Propiedades de ab-desorción de hidrógeno del intermetálico Mg<sub>2</sub>Ni obtenido empleando un molino de bolas Simoloyer*

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### Abstract

Intermetallic Mg<sub>2</sub>Ni was produced from elemental powder blends by mechanical alloying in a batch scale using a rotary horizontal mill (Simoloyer). Fast hydrogenation kinetics are obtained: 2.2 wt.% of hydrogen is absorbed within 10 minutes at 300 °C. Hydrogen sorption kinetics were further improved by adding Pd (1 mol%) powder as a catalyst during ball milling. Crack formation and concomitant particle size reduction was observed by scanning electron microscopy after hydrogen cycling, which is attributed to internal stresses in the particles.

**Keywords:** High-energy ball milling (Simoloyer), hydrogen storage, particle size evolution.

### Resumen

Se produjo por aleación mecánica el compuesto intermetálico Mg<sub>2</sub>Ni a partir de polvos elementales, empleando un molino de alta energía (producción por lotes) horizontal rotatorio comercialmente conocido como Simoloyer. Se observó que este compuesto presentaba una rápida absorción de hidrógeno, en donde se obtuvo 2.2 % peso de hidrógeno a 300 °C después de 10 minutos de proceso. La cinética de absorción de hidrógeno se mejoró al

agregar 1 % mol de paladio durante la molienda. Se observaron por microscopía electrónica de barrido, grietas y disminución del tamaño de partícula por efecto de los ciclos de absorción-desorción de hidrógeno; y los cuales se atribuyeron a esfuerzos internos en las partículas.

**Descriptores:** molienda de bolas de alta energía (Simoloyer), almacenamiento de hidrógeno, evolución del tamaño de partícula.

## Introduction

Mechanical alloying (MA) yields chemically homogeneous alloys (Benjamin, 1976), ( Benjamin *et al.*, 1974), (Koch, 1989), (Bormann, 1977) with extremely fine crystallite sizes. The process is characterized by high-energy impact collisions of the milling tools, which lead to plastic deformation, cold-welding, and particle fracture which provides the driving force for microstructural refinement. Different techniques are available to conduct MA on the laboratory scale. However, few types of equipment have been designed to obtain larger quantities of powder for industrial production, such as horizontal rotary ball mills (Simoloyer model CM100s) (Zoz *et al.*, 1996, 1999). The charge-discharge operations in this equipment can either take place under inert gas or vacuum to prevent oxidation. The milling chamber of this mill is designed such that allows vials cooling using either liquid or gas media. Magnesium and magnesium-based alloys have been widely studied as hydrogen storage materials by many research groups (Zaluzski *et al.*, 1995), (Liang *et al.*, 1999), (Zaluski, 1995), (Zaluski *et al.*, 1999), (Kumar *et al.*, 1995) because of their high hydrogen storage capacities by weight (7.6 wt.% of MgH<sub>2</sub> and 3.6 wt.% of Mg<sub>2</sub>NiH<sub>4</sub>), long-term stability, full reversibility and low raw materials costs. A technological breakthrough regarding reaction kinetics has been achieved by preparing nanocrystalline alloys by high-energy milling and by adding suitable catalysts, e.g., metal additives (Zaluzski *et al.*, 1995), (Liang *et al.*, 1999) or more recently, metal oxides (Oelerich *et al.*, 2001), (Youp *et al.*, 2002), (Inui *et al.*, 2002). For example, Zaluski *et al.* (1995) used elemental Pd as catalyst and stored about 2.5 wt.% of hydrogen in Mg<sub>2</sub>Ni at 200°C/15bar in 10 minutes. For MgH<sub>2</sub> with oxide catalysts, 80% of the theoretical capacity, *i.e.*, 6.1 wt.% was obtained at 300°C/8 bar in 5 minutes (Oelerich, 2001). So far, all studies related to nanocrystalline hydrides were based on materials produced in small milling machines on the laboratory scale. For prototype purposes and technical applications, larger quantities are required.

However, respective studies regarding upscaling of the powder production are still lacking.

## Experimental procedure

Elemental powder blends (Mg JCPDF-35-0821, Ni JCPDF-04-0850) corresponding to the stoichiometric ratio for the intermetallic Mg<sub>2</sub>Ni phase were milled in a high-energy rotary ball mill (Simoloyer model CM01-2l, Zoz GmbH Germany). These results are already obtained and publication is available (Martínez *et al.*, 2006). Different ball-to-powder mass ratios were used to evaluate efficiency of the mill system and samples without catalyst were stored for several months before measuring hydrogen sorption properties. Palladium powder (1 mol%) was added as a catalyst in a sample with a mass ratio of 10:1, for comparing hydrogen sorption kinetics with the powders without catalyst.

For measurements of hydrogen absorption kinetics, sample holders were sealed inside a glove box and attached to a hydrogen titration apparatus, which was specially designed (Schulz *et al.*, 1999) for fast data acquisition.

Particle morphology during milling, as well as, after hydrogen charging and discharging was investigated by SEM (JEOL JSM-35CF). Contamination by oxygen and iron was quantified using energy disperse spectrometry (EDS) available in the SEM.

## Results and discussion

Mechanical alloying using the Simoloyer ball mill

The XRD patterns for different ball-to-powder mass ratios as a function of milling time are shown in figure 1. Peak broadening indicates microstructural refinement. The crystallite size of Mg<sub>2</sub>Ni is estimated between 4 and 11 nm using the Scherrer-formula (Cullity, 1978). Peaks corresponding to the intermetallic Mg<sub>2</sub>Ni (JCPDF-35-1225, mainly diffracted between 20°-22° and 40°-45°) are observed after different milling times depending on the mass ratio. Traces of Ni were found

in all milling experiments and unreacted Mg was only found for a mass ratio of 50:1. These results show that  $Mg_2Ni$  formation strongly depends on the mass ratio. Increasing the mass ratio considerably reduces the  $Mg_2Ni$  synthesis time from 25 hours down to 4 hours using mass ratios of 10:1 and 100:1, respectively.

In all milling process the possibility exists of contamination due to wear of media (balls) and control process

(atmosphere). Analysis of possible contaminants such as chromium, iron and oxygen by using energy dispersive spectrometry (EDS) were carried out.

EDS measurements showed only the presence of iron and oxygen as is reported in table 1 for all ball-to-powder mass ratios. The numbers in brackets indicate the milling time of the sample. Average and corresponding deviations of all measurements are reported.

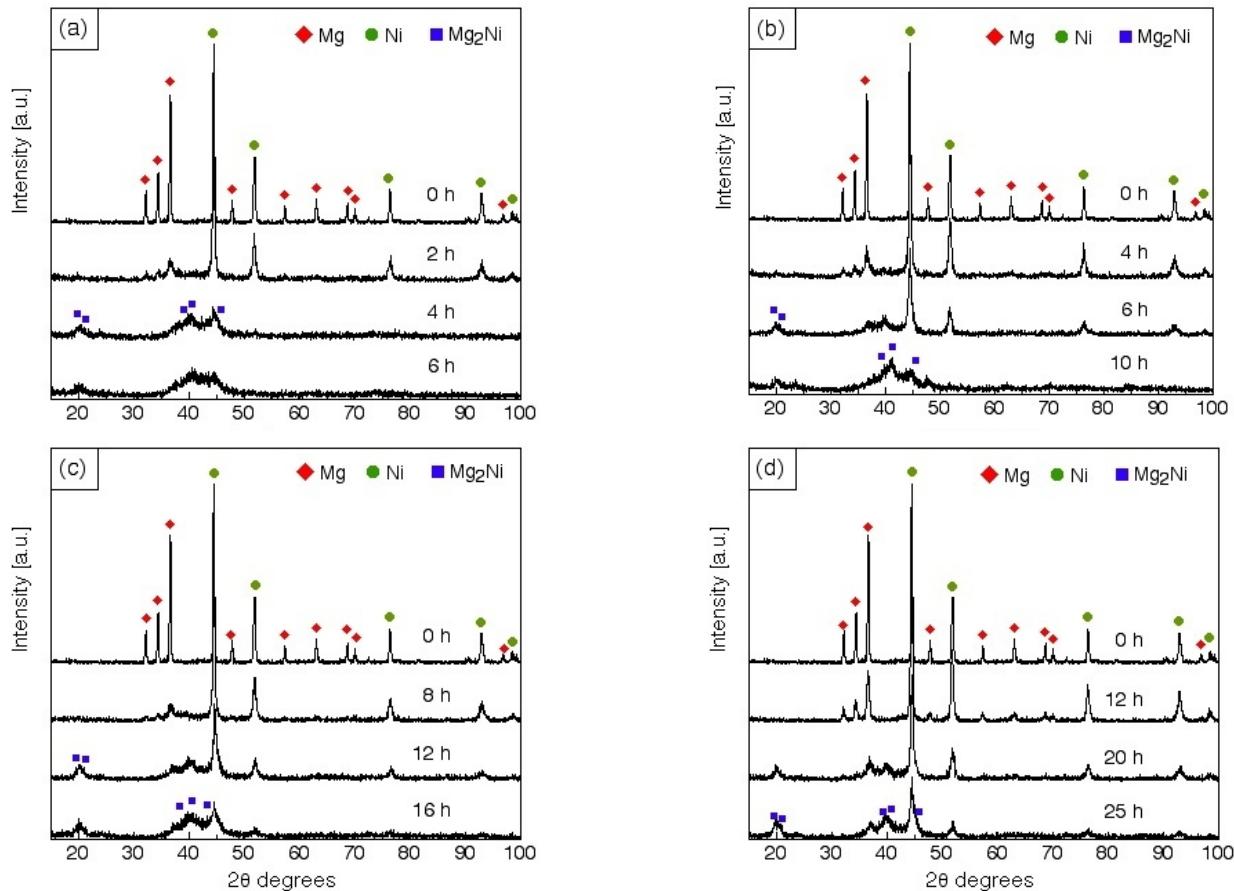


Figure 1. XRD patterns for Mg-Ni powders milled for several times with different ball-to-powder mass ratios:  
 (a) 100:1, (b) 50:1, (c) 20:1, (d) 10:1

Table 1. Iron and oxygen contamination after milling

| Mass ratio | Average Fe (wt.%) |      | Average O (wt.%) |      |
|------------|-------------------|------|------------------|------|
| 100:1 [6h] | 1.6               | 0.2  | 5.1              | 0.1  |
| 50:1 [10h] | 0.8               | 0.2  | 4.3              | 0.05 |
| 20:1 [16h] | 0.4               | 0.15 | 5.6              | 0.06 |
| 10:1 [25h] | 0.4               | 0.2  | 4.9              | 0.1  |

Iron and oxygen contamination took place from the vial's erosion and air when samples were taken for characterization. Even though the milling time required for complete transformation into the  $Mg_2Ni$  phase is much shorter for a mass ratio of 100:1, the highest iron contamination was detected in this sample. This is attributed to the smaller powder quantity and therefore, more impacts collisions of the balls. The oxygen contamination is similar (approximately 5 wt.%) for all specimens independently of the mass ratios, which indicates contamination due to handling for sampling to analysis.

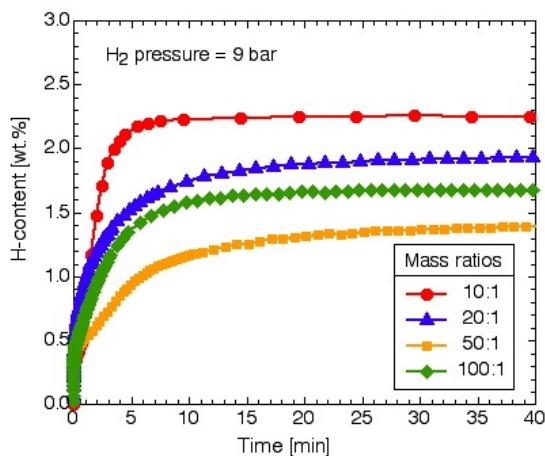


Figure 2. Hydrogen absorption properties at 9 bar and 300 °C for  $Mg_2Ni$  milled with different mass ratios

## Hydrogen storage properties

### Sorption properties of $Mg_2Ni$ without catalyst

The hydrogen reaction kinetics at 9 bar hydrogen pressure and 300°C of the intermetallic  $Mg_2Ni$  obtained with different ball-to-powder mass ratios is shown in figure 2. Absorption kinetic is best for the mass ratio of 10:1 and 2.2 wt.% of hydrogen is absorbed within 10 minutes at 300°C. It is observed that increasing mass ratios hydrogen absorption kinetics is lower, with exception of the mass ratio of 50:1. According to our previously work (Martínez *et al.*, 2006), if is taken into account only the iron content, the sample with mass ratio of 100:1 should present the lower kinetic and hydrogen capacity, but in the sample with mass ratio of 50:1 Mg-traces still present after milling which can easily forms an oxide layer which inhibits the reaction with the hydrogen.

Due to its highest hydrogen absorption capacity, the powder milled with the mass ratio of 10:1 was used for further kinetics characterization. Absorption-desorption curves at different temperatures are shown in figure 3.

As expected, the best absorption kinetics are achieved at 300°C, taking about 10 minutes for completion. At lower temperatures, the absorption kinetics slow down and the maximum hydrogen storage is achieved only after 90 minutes at 250°C. There is no significant difference observed between desorption at 300°C and 250°C and is completed after 12 minutes for both temperatures.

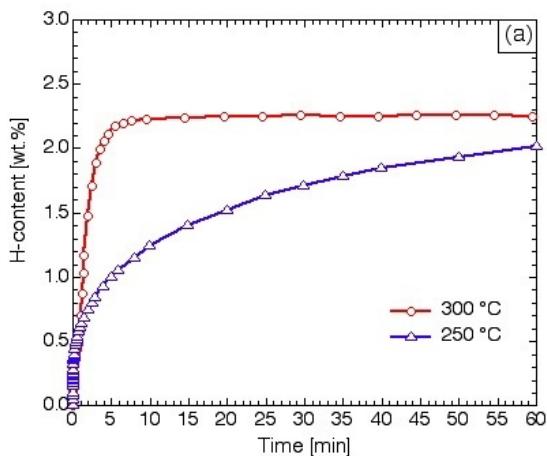
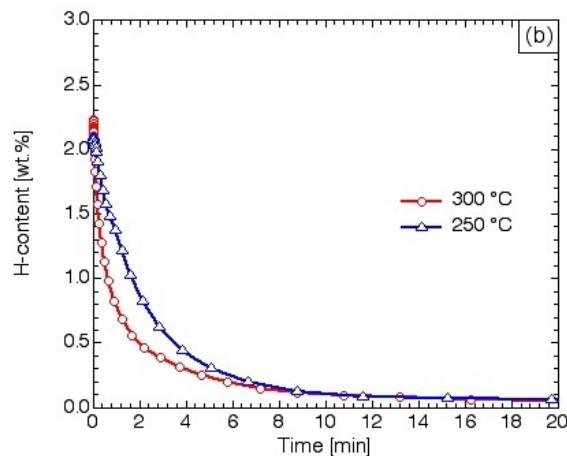


Figure 3. Hydrogen sorption properties at different temperatures for  $Mg_2Ni$  milled with a mass ratio of 10:1 (a) absorption at 9 bar, (b) desorption curves



### Sorption properties of $Mg_2Ni$ with catalyst

The absorption and desorption curves of  $Mg_2Ni + Pd$  (1 mol%) are presented in figure 4. Absorption kinetics were enhanced in comparison to the material without catalyst, and the total capacity (after 90 minutes) was about 3.0 wt.%, which is very close to the results obtained by Klassen *et al.* (1998) for similar material. Full desorption was achieved after 2 and 8 minutes for 300 and 250°C, respectively. Comparing with the results for  $Mg_2Ni$  without catalyst, desorption kinetics was about five times faster at 300 °C. These results demonstrate the enhancement of the sorption properties by adding Pd as a catalyst. The catalytic effect of Pd suggested by Zaluski *et al.* (1999) is due to small Pd particles distributed on the metal surface. They process is explained by a “spill-over” phenomenon: hydrogen is easily chemisorbed i.e. dissociated on the Pd-surface and

migrates to the base storage material, i.e. Mg, which does not show easy chemisorption of hydrogen. Although no direct evidence is reported in this work, is suggested that high-energy ball milling by using a Simoloyer produces very fine Pd particles and/or disperses Pd-clusters on the powder surface and absorption-desorption kinetics are improved.

As was reported previously (Martínez *et al.*, 2006) particle size decrease upon increasing milling time. The average particle size before milling was in the range of 40-50  $\mu m$ , and reduces to 5-20  $\mu m$  after 25 hours milling time when a ball-to-powder mass ratio of 10:1 is used. Figure 5 shows backscattered electron images of powders milled at 8 and 25 hours with a mass ratio of 10:1. While Mg-rich and Ni-rich areas can still be distinguished after 8 hours, the powder appears mostly homogeneous after 25 hours milling.

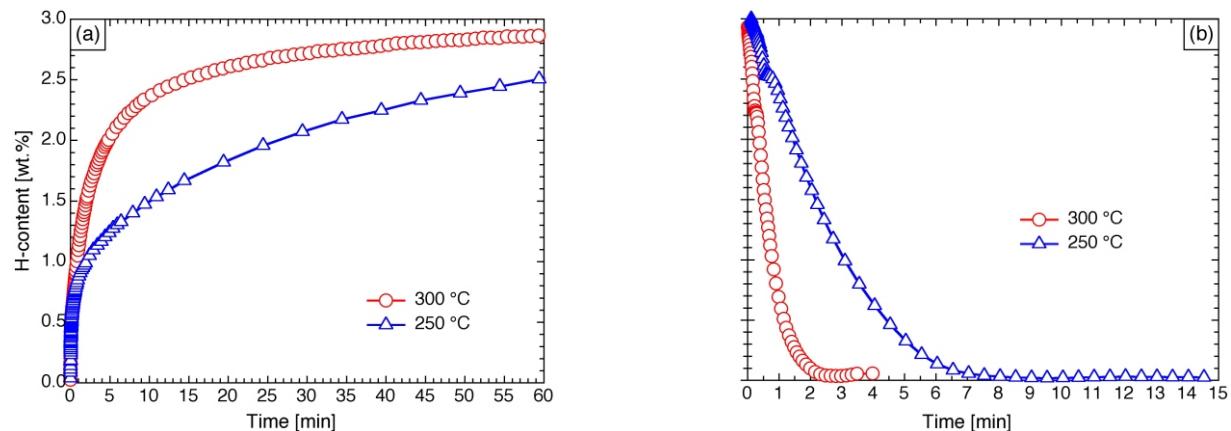


Figure 4. Hydrogen sorption properties at different temperatures of  $Mg_2Ni + 1\% \text{mol Pd}$  milled with a mass ratio of 10:1. (a) absorption at 9 bar and (b) desorption curves

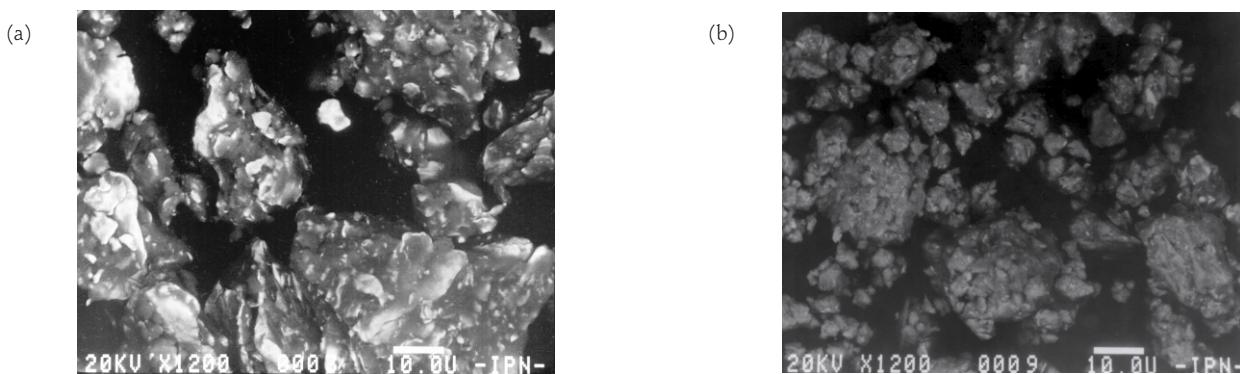


Figure 5. Microstructural evolution during milling of Mg-Ni with a mass ratio of 10:1 (a) 8 h milling time, (b) 25 h milling time

Figure 6 shows SEM pictures of the Mg<sub>2</sub>Ni with catalyst (mass ratio of 10:1) after the second absorption measurement and after six ab-desorption cycles. It is shown cracking of agglomerates and particles. We suppose that exists an effect of the internal stresses in particles built up during hydrogenation-dehydrogenation process (Mg<sub>2</sub>Ni+2H<sub>2</sub> → Mg<sub>2</sub>NiH<sub>4</sub>). Regarding to this effect, Inui and co-workers (2002) reported that for some materials, the particle size decreases during absorption-desorption cycling because of internal stresses caused by lattice expansion-contraction, which is a good agreement with our results. Although reticular parameters were not calculated, and considering cell expansion-contraction, is supposed that theoretically the cell volumes of an hcp (Mg<sub>2</sub>Ni) and fcc (Mg<sub>2</sub>NiH<sub>4</sub>) crystal

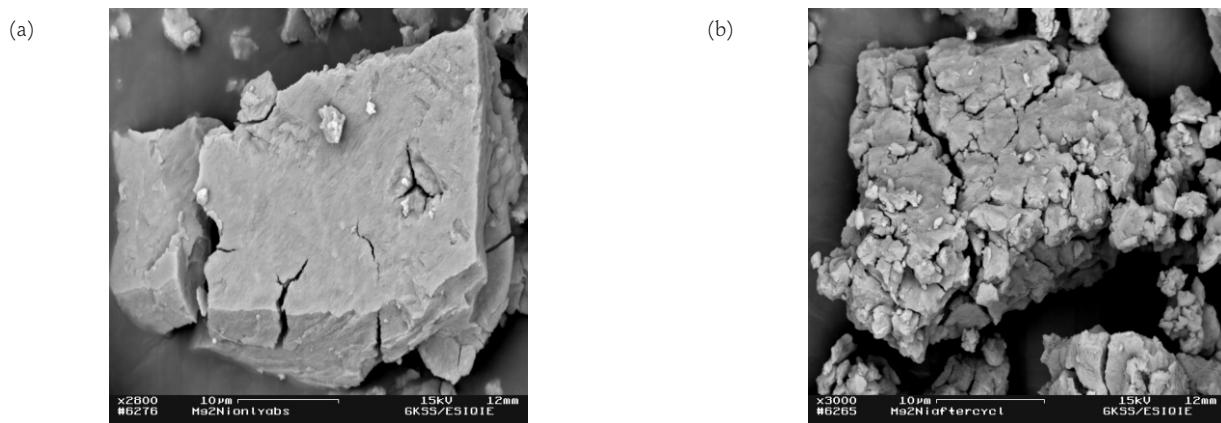


Figure 6. Mg<sub>2</sub>Ni particles with: (a) only absorption in the second absorption cycle, (b) after 6th absorption-desorption cycle

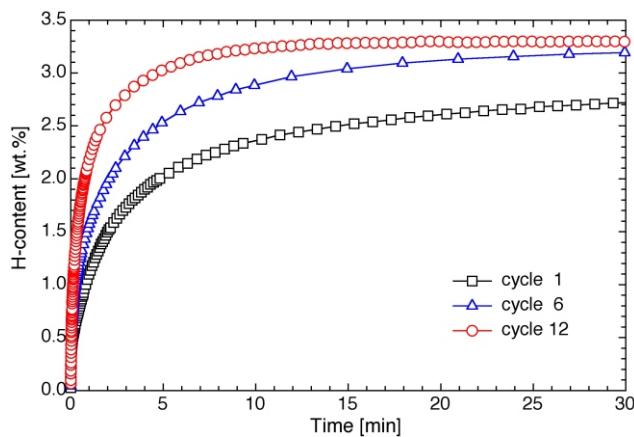


Figure 7. Hydrogen absorption cycling of a sample with Pd-catalyst at 300 °C/9 bar

structures are 311 and 278, respectively; therefore, distortion of cell is evident and our experimental results are also in good agreement with this consideration.

Cracks are formed and some smaller particles break loose, exposing fresh surfaces that are beneficial for improving the reaction with hydrogen. A sample with Pd as catalyst was cycled at 300°C/ 9 bar hydrogen pressure and results of the absorption process is shown in figure 7.

As is shown in figure 6, “fresh” surfaces generated during hydrogen cycling improves hydrogen absorption process (figure 7). Hydrogen content of 3.3 wt. % is obtained after 15 minutes in a sample with 12 cycles; which is near to the theoretical capacity, 3.6 wt. %, for the reaction Mg<sub>2</sub>Ni+2H<sub>2</sub> → Mg<sub>2</sub>NiH<sub>4</sub>.

## Conclusions

1. Material stored in glass vial under argon atmosphere for several months (Mg<sub>2</sub>Ni without catalyst) shows fast absorption kinetics at 300°C (15 minutes for complete absorption), although its capacity is rather low (2.2 wt. %). Full desorption of Mg<sub>2</sub>Ni without catalyst is readily achieved at 250°C in about 10 minutes in vacuum.
2. Small amounts of Pd used as a catalyst (1 mol%) further improve the hydrogen sorption kinetics. Full desorption at 300°C was achieved after 2 minutes.
3. The average particle size decreases with increasing milling time, and a further decrease due to particle cracking was observed during cycling.

4. Hydrogen ab-desorption cycles produces internal stresses and generated new surfaces that improve hydrogenation process.

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### References

Benjamín J.S. Scientific American. Vol. 234. 1976. Pp. 40-48.

Benjamin J.S., Volin T.E. Metallurgical Transactions A. Vol. 5. 1974. Pp. 1929-1934.

Koch C.C. *Material Synthesis by Mechanical Alloying*. Annual Review of Materials Science. Vol. 19. 1989. Pp. 121.

Bormann R. Mat. Sc. and Eng. Vol. A226-228. 1997. Pp. 268-273.

Zoz H., Ernst D., Weiss H., Magini M., Powel C., Suryanarayana C., Froes F.H. *Fachzeitschrift METALL*. Vol. 50. 1996. Pp. 575-579.

Zoz H., Ren H., Reichardt R., Benz H.U. Vol. 1, No. 1. 1999. Pp. 15-19.

Zaluzski L., Zaluska A., Ström-Olsen J.O. *Journal of Alloys and Compounds*. Vol. 217. 1995. Pp. 245-249.

Liang G., Huot J., Boily S., Van-Neste A., Schulz R. *Journal of Alloys and Compounds*. Vol. 292. 1999. Pp. 247-252.

Zaluski L., Zaluska A., Tessier P., Ström-Olsen J.O., Schulz R. *Journal of Alloys and Compounds*. Vol. 217. 1995. Pp. 295-300.

Zaluzski L., Zaluska A., Ström-Olsen J.O. *Journal of Alloys and Compounds*. Vol. 288. 1999. Pp. 217-225.

Kumar-Singh A., Kumar-Singh A., Srivastava O.N. *Journal of Alloys and Compounds*. Vol. 227. 1995. Pp. 63-68.

Oelerich W., Klassen T., Bormann R. *Journal of Alloys and Compounds*. Vol. 315. 2001. Pp. 237-242.

Youp M., Jean-Louis B., Darriet B. *Journal of Alloys and Compounds*. Vol. 340. 2002. Pp. 256-262.

Inui H., Yamamoto T., Hirota M., Yamaguchi M. *Journal of Alloys and Compounds*. Vol. 330. 2002. Pp. 117-124.

Martinez-Franco E., Klassen T., Bormann R., Jarmillo D. *Materials Science Forum*. Vol. 509. 2006. Pp. 141-145.

Schulz R., Boily S., Hout J. Canadian patent. Ser.-Nr.: 2207149. 1999.

Cullity B.D. *Elements of X-ray diffraction*. 2nd. Ed. Addison-Wesley Publishing. USA. 1978.

Klassen T., Oelerich W., Zeng K., Bormann R. *Magnesium Alloys and their Applications*. Ed. by Mordike B.L., Kainer K.U. Werkstoff-Informationsgesellschaft GmbH, Frankfurt. 1998. Pp. 307-311.

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