



# Catalysed reactive milling

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## Abstract

Magnesium is mechanically activated in a high-energy planetary ball mill. It is found that the yield of magnesium hydride is considerably increased by the addition of a small amount of nickel. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Catalysis; Ball-milling; Hydrogen; Magnesium; Nickel

## 1. Introduction

Magnesium-based alloys are promising materials for safe and practical hydrogen storage. However their kinetic properties are poor and the hydrides they form are too stable. It has been found that mechanical alloying or grinding can significantly improve the kinetic properties of magnesium-based alloys [1].

Magnesium hydride had been synthesised by reactive milling [2,3]. It is interesting to note that magnesium hydride can be formed at room temperature and moderate pressure by milling, while conventional synthesis by gas–solid reaction requires high temperatures (>600 K) and pressures (about 5 MPa). However the reaction proceeds much more slowly than for other hydride forming metals. The addition of nickel to improve the kinetic properties of magnesium has already been investigated [4,5]. However they looked at the catalytic effect of Pd [1] and Ni [4,5] on gas–solid reaction of the Mg–H system AFTER milling, while we study the catalytic effect of nickel DURING the milling process, using chemical analysis and X-ray diffraction to characterise our ball-milled materials.

## 2. Experimental procedure

Milling experiments were carried out in a Kurimoto planetary ball mill with a rotational speed of 885 rpm. The vials had an internal diameter of 50 mm and an internal height of 94 mm. The amount of powder put in the vials

was 7.000 g and 40 stainless steel balls (7mm diameter) were used. Magnesium (99.9%) and nickel (99.9%) were weighed to a precision of 0.001 g. A valve permitted the evacuation of air from the milling vials and the introduction of hydrogen. The vials were sealed with rubber o-rings. In this article, experiments were conducted under 0.5 MPa of hydrogen (99.99999% purity). The hydrogen was introduced prior to milling; no exchange of gas was done during milling.

The X-ray diffraction experiments were performed using CuK $\alpha$  radiation in a Rigaku Geigerflex diffractometer. The patterns were analysed using the Rietveld method [6,7]. We refined the lattice, thermal, asymmetry, preferred orientation, and instrument-related parameters, as well as the broadening due to crystallite size reduction and strain. We used the space groups and atomic positions given in the literature [8,9].

The hydrogen content of selected samples was measured using a LECO H<sub>2</sub> analyser, in which the sample is melted and the amount of hydrogen is determined by measuring the thermal conductivity of the gas, which is much higher than all other reactive gases. The uncertainty is 1% of the measured value.

## 3. Results and discussion

We milled pure Mg powders under 0.5 MPa of hydrogen gas for 1, 2, 5, 10, 20 and 40 h. The amount of hydrogen in the vial is approximately one fourth of the theoretical absorption capacity of the sample. We observed that magnesium had a strong tendency to stick to the balls and walls of the milling vial. The X-ray patterns of the starting materials and the sample milled 40 h are shown in Fig. 1.

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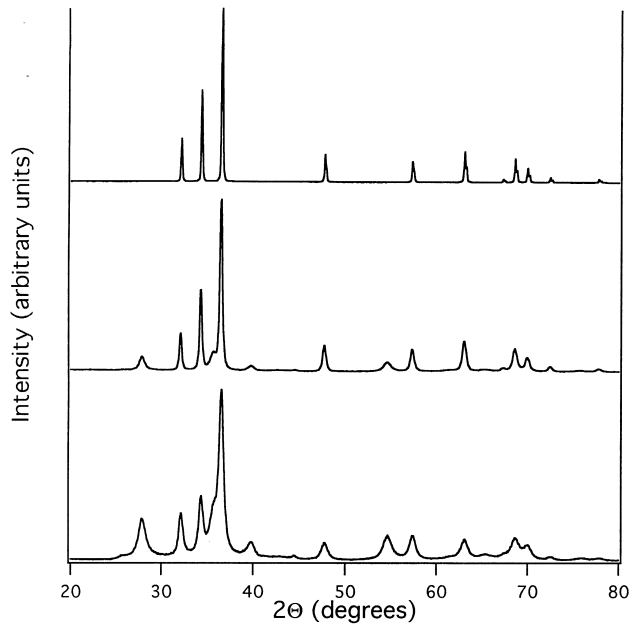


Fig. 1. X-ray diffraction patterns of Mg before milling (top), Mg milled 40 h (centre), and Ni-doped Mg milled 40 h (bottom).

The patterns of all samples were analysed by the Rietveld method [4,5]. The patterns exhibit peak broadening due to crystallite size reduction and deformation. The average crystallite size of magnesium is 60 nm and that of magnesium hydride is 20 nm. The strain level of both phases is high, generally above 5%. The milled magnesium phase has a slightly smaller unit cell than pure Mg. Part of the magnesium is transformed into magnesium hydride during milling. The lattice parameters of milled magnesium are  $a=3.2079\pm 0.0003$  Å and  $c=5.2075\pm 0.0006$  Å. The values for our magnesium powder prior to milling are  $a=3.2089\pm 0.0002$  Å and  $c=5.2094\pm 0.0002$  Å. The amount of hydride phase estimated using Rietveld analysis, is shown in Fig. 2. We also calculated the amount of the hydride phase (Fig. 3) from the hydrogen content mea-

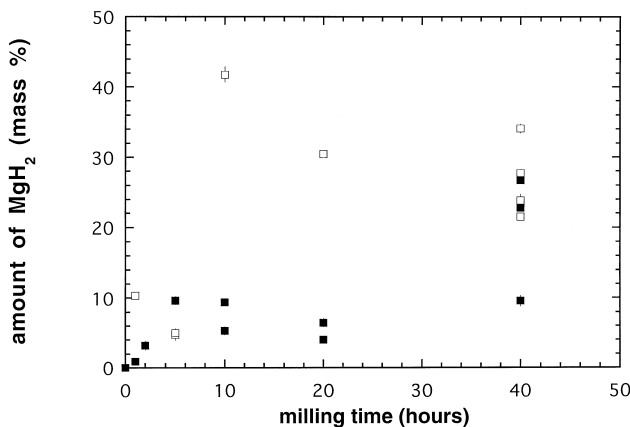


Fig. 2. Weight fraction of  $\text{MgH}_2$  as a function of milling times for pure Mg (solid squares) and Ni-doped Mg (empty squares), as determined by Rietveld analysis.

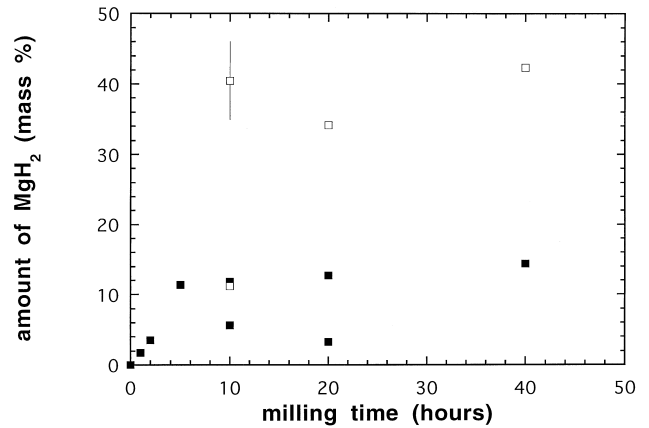


Fig. 3. Weight fraction of  $\text{MgH}_2$  as a function of milling times for pure Mg (solid squares) and Ni-doped Mg (empty squares), as determined by the Leco  $\text{H}_2$  analyser.

sured with the LECO  $\text{H}_2$  analyser. The two methods give similar results. The lattice parameters of the hydride phase are  $a=4.5185\pm 0.0008$  Å and  $c=3.013\pm 0.005$  Å compared to the reference values of  $a=4.5198\pm 0.0007$  Å and  $c=3.0250\pm 0.0006$  Å [9].

From Fig. 3, it can be seen that before 20 h of milling the amount of hydride phase varies in a somewhat erratic manner. We believe this is due the fact that magnesium rapidly sticks to the walls of the vial at the start of the milling process, then falls off in an unpredictable manner. At 40 h however the results are reproducible.

If we change the initial composition to include one atomic % of nickel, the transformation to the hydride phase is considerably faster (Figs. 1–3). Moreover the amount of powder recovered at the end of the milling process is one order of magnitude larger. In most experiments, the amount of powder recovered from the vial without excessive scraping is of the order of 100 mg. In the case of  $\text{Mg}_{99}\text{Ni}_1$  milled 20 and 40 h, we obtain about one gram of fine powder.

At intermediate milling times, the amount of nickel phase obtained from Rietveld analysis of the X-ray pattern is sometimes considerably larger than 1%. We think this supports the idea that the erratic variations in the amount of hydride during milling are due to the inhomogeneity of the milling charge at intermediate milling times.

In some cases, the final amount of hydride phase apparently exceeds the limit of 25% expected for the amount of hydrogen injected into the vial before milling. This might be due to a hydrogen concentration lower than two hydrogen per formula unit in the hydride phase, or to the presence of an amorphous phase, which is not taken into account in the Rietveld analysis.

The unit cell of magnesium and that of the hydride phase in the nickel-doped sample are slightly contracted compared to the nickel-free sample, the lattice parameters being  $a=3.204\pm 0.001$  Å and  $c=5.202\pm 0.002$  Å for Mg, and  $a=4.514\pm 0.002$  Å and  $c=3.007\pm 0.004$  Å for  $\text{MgH}_2$ .

Preliminary absorption–desorption experiments on these samples show good kinetic properties, which is not surprising for ball-milled materials, some of which are doped with nickel, whose catalytic effect is well known [4,5].

#### 4. Conclusion

Nickel is an effective catalyst for the synthesis of magnesium hydride by the reactive milling of magnesium powder under hydrogen atmosphere. Nickel-doped powder samples contain significantly more hydride phase than pure magnesium samples. The effectiveness of nickel is especially evident when one compares the amount of powder ultimately recovered from nickel-free and nickel-doped samples.

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