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# Ball Milling under Reactive Atmosphere

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## Introduction

Ball milling is one of the promising techniques to not only improve hydrogenation properties of hydrogen absorbing alloys, but also to form novel hydrides under various atmospheres, as Profs. Orimo and Fujii reported [1]. Reactive milling (milling under hydrogen) of hydrogen absorbing alloys has many possibilities, such as to produce hydrides at low temperatures, to form hydrides whose alloy phase is not stable (e. g., $Mg_2FeH_6$) and to obtain various products by changing reaction conditions (e. g., available H/M inventory in the milling pot, hydrogen pressure, milling energy, etc.).

The purpose of this project is to clarify the conditions that determine the products of reactive milling of $Mg_2Ni$. The milled products and their crystal structure, particle size, lattice strain, etc., will be investigated as functions of hydrogen-to-metal ratio, hydrogen pressure and milling energy.

## Experimental

Milling experiments were carried out in a Fritsch planetary mill, P-5, and a Kurimoto planetary mill, HG-BX254E. In all cases, the amount of alloy put in the pots was $4.000 \pm 0.001$ g and 40 steel balls (7mm diameter) were used. The $Mg_2Ni$ alloy was purchased from Furukawa Magnesium Company. The phase composition of the alloy is 90.2% $Mg_2Ni$, 5.9% Mg, and 3.8 % $MgNi_2$ [2]. A valve permitted the evacuation of air from the milling pots and the introduction of gases. The pots were sealed with rubber o-rings. Experiments were conducted either under hydrogen atmosphere (99.99999 % purity) or vacuum. The hydrogen was introduced prior to milling; no exchange of gas was done during milling.

## Results and Discussion

Professors Orimo and Fujii reported that the products of ball milled $Mg_2Ni$ under hydrogen were distorted $Mg_2Ni$ hydride at inter-gain regions and nanocrystalline $Mg_2Ni$ at intra-grain regions [1]. However, the available H/M inventory in the milling pot was less than the stoichiometric value, 1.33.

We obtained very different results by milling of $Mg_2Ni$ under hydrogen (Figure 1). Our first such experiments were done under hydrogen at 1.0 MPa. At this pressure, the amount of hydrogen, contained in the pot, represents 3.64 weight % of the sample ($Mg_2Ni$ + $H_2$). This is slightly more than the amount of hydrogen in $Mg_2NiH_4$. We noticed, however, that there was still some hydrogen gas in the pot after 10 hours of milling. We did not expect, therefore, to obtain a completely hydrogenated sample.

In the first 30 minutes of milling, $Mg_2Ni$ absorbs hydrogen and the unit cell expands. Upon further milling, the intensities of $Mg_2Ni$ peaks decrease while peaks belonging to a hydride phase appear. The shape of the peak close to 24 degrees at 5 hours of milling suggests that it is, in fact, a superposition of two peaks, namely the (111) and (131) peaks of the low-temperature $Mg_2NiH_4$ structure [3]. At 10 hours the peak is somewhat more symmetric.

There is a broad range of intensity not accounted for by the crystalline phases between 40 and 45 degrees. We fitted the intensity between 34 and 50 degrees with three Lorenztian peaks (Figure 2): two relatively narrow peaks for the superposed peaks of the crystalline phases of the high-temperature phase and the low-temperature phase. The third peak is a very broad one used to mimic the intensity from an amorphous phase. This intensity, due to an amorphous fraction, was subtracted from the total experimental intensity pattern. The Rietveld analysis of this "corrected" pattern is considerably better than that of the as-measured pattern. The relative weight fraction of crystalline phases remains 30% high-temperature phase and 70% low-temperature phase. The chemical analysis (ICP) on the final sample gave the following results: Mg 44.7 weight %, Ni 54.2, Fe 0.87. The same analysis on the starting material gave: Mg 44.2, Ni 55.7, Fe 0.02.
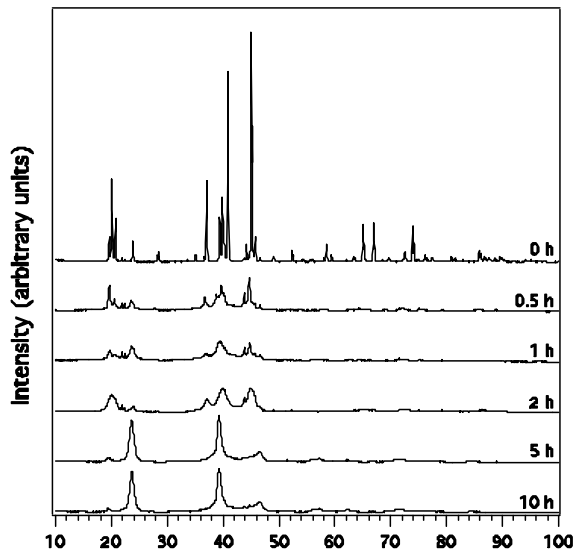


**Figure 1. X-ray diffraction pattern (CuKα) of $Mg_2Ni$ milled under 1.0 MPa of hydrogen for 0, 0.5, 1, 2, 5, and 10 hours.**
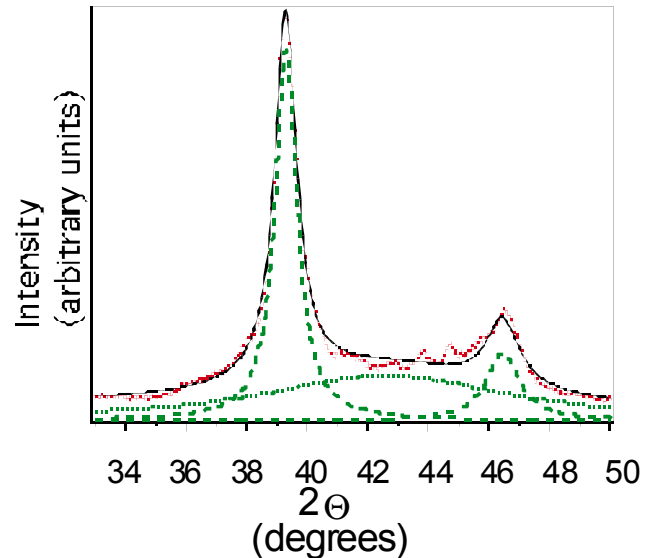


**Figure 2. Mathematical fit of the X-ray pattern of $Mg_2Ni$ milled under 1.0 MPa of hydrogen for 10 hours (solid line) using two narrow peaks (dashed lines) for the crystalline phases and a broad peak (dotted line) for the intensity due to an amorphous phase.**

The hydrogen content of the sample milled for 10 hours, measured using a LECO $H_2$ analyzer, is 2.8 wt% compared to 3.6 wt% for $Mg_2NiH_4$. For the unit cell of the low-temperature structure we find the following lattice parameters: $a$ = 1.445 ± 0.003 nm, $b$ = 0.643 ± 0.001 nm, $c$ = 0.652 ± 0.001 nm. The values for well crystallized low-temperature $Mg_2NiH_4$ are 1.4363 nm, 0.64052 nm, and 0.64863 nm, respectively [3]. For the high-temperature structure we find $a$ = 0.650 ± 0.001 nm compared to 0.6490 nm, reported in [4]. Larger lattice parameters for nanophase materials compared to coarse-grained ones are often reported. The average size of $Mg_2Ni$ crystallites is approximately 10 nm. This value is obtained from the broadening of the X-ray peaks determined by Rietveld analysis and from dark field transmission electron micrographs.

In the milling experiment at 1.0 MPa of hydrogen, the possible stabilization of the high-temperature $Mg_2NiH_4$ structure is particularly interesting in light of previously found evidence that hydrogen has higher mobility in it than in the low-temperature structure [5]. A more immediate result of this experiment is the production of an already-charged metal hydride with high hydrogen content that, therefore, should not require a lengthy activation treatment prior to being used in a storage device. The fine microstructure also represents a definite advantage in terms of kinetic properties.

We also milled $Mg_2Ni$ under 0.5 MPa of hydrogen. This experiment produced a composite material consisting of 70 weight % $Mg_2Ni$ structure with hydrogen in solid solution and 30 weight % low-temperature $Mg_2NiH_4$. The lattice parameters of the $Mg_2Ni$ structure present in the sample milled for 10 hours are: $a$ = 0.525 ± 0.001 nm and $c$ = 1.340 ± 0.002 nm. These are very close to the values found for $Mg_2NiH_{0.3}$, specifically, $a$ = 0.52315 nm and $c$= 1.3404 nm. By comparison, the lattice parameters of $Mg_2Ni$ are: $a$ = 0.52107 nm and $c$= 1.32437 nm [6]. The amorphous phase that was found in the X-ray Patterns would likely contain hydrogen and may account for the difference between the amount of hydrogen determined by the LECO $H_2$ analyzer (1.7 weight %, which is close to the 1.82 % contained in the pot at the onset of the milling experiment) and the amount contained in the low-temperature $Mg_2NiH_4$ structure (approximately 1.0 weight%, assuming perfect stoichiometry) plus the amount dissolved in $Mg_2Ni$ (around 0.2 weight % of the sample, assuming a composition $Mg_2NiH_{0.3}$ for that structure). The conditions of this experiment are very similar at least as far as hydrogen pressure and composition are concerned, to those of reference [1], where the formation of a disordered phase is claimed. We find no evidence for the formation of a disordered phase - our X-ray results are satisfactorily described by a mixture of $Mg_2NiH_{0.3}$, low-temperature $Mg_2NiH_4$ structure, and a minority Mg-Ni-H amorphous phase.

We compared the milling products of two mills. The nominal maximum milling energy of HG-Bx254E is 160$g$, which is ten times as much as that of P-5. After several milling experiments, it was found that milling power did not influence the products, but instead only shortened the milling time.

**Conclusion**

The products of the present experiments are well-crystallized hydrides of $Mg_2Ni$ and the amorphous phase. The milling power does not affect the hydrogenation products.

**References**

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