

# NANOCRYSTALLINE HYDROGEN ABSORBING Mg-Ni ALLOY PROCESSED BY MECHANICAL (BALL) MILLING

J. Bystrzycki<sup>1</sup>, T. Czujko<sup>1</sup>, R. A. Varin<sup>2</sup>, D. Oleszak<sup>3</sup>, T. Durejko<sup>1</sup>, W. Darlewski<sup>4</sup>,  
Z. Bojar<sup>1</sup> and W. Przetakiewicz<sup>1</sup>

<sup>1</sup>) Institute of Materials Technology and Applied Mechanics, Military University of Technology, Kaliskiego 2, 00-908 Warsaw 49, Poland

<sup>2</sup>) Department of Mechanical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 2G1

<sup>3</sup>) Faculty of Materials Science and Engineering, Warsaw University of Technology, Woiowska 141, 02-507 Warsaw, Poland

<sup>4</sup>) Institute of Chemistry, Military University of Technology, Kaliskiego 2, 00-908 Warsaw 49, Poland

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**Abstract.** A nearly single-phase Mg<sub>2</sub>Ni alloy obtained by ingot metallurgy was mechanically (ball) milled for 20 h in two types of ball mills: Fritsch and Spex with the objective of obtaining nanocrystalline powders suitable for subsequent hydrogenation in gaseous hydrogen. The powders processed in both ball mills are characterized by quite similar average powder particle size which is within the range of 1-30 μm and the average nanograin size of the Mg<sub>2</sub>Ni phase which is on the order of 7 nm as roughly estimated from the Scherrer formula. However, X-ray diffraction (XRD) spectrum from the Spex powder gives some evidence of partial amorphization of the Mg<sub>2</sub>Ni phase as opposed to the Fritsch powder. Hydriding tests of both powders investigated in an automated Sieverts apparatus have shown that the Fritsch powder exhibits faster hydriding kinetics than its Spex counterpart. The overall kinetics of hydrogen sorption for the faster absorbing Fritsch powder seems to be roughly in the same range as reported in the literature since it absorbs about 2.7 wt.% of hydrogen after 1800 s (30 min). The differences in the hydriding kinetics between the Fritsch and Spex powders are discussed in terms of the presence of the partially amorphized Mg<sub>2</sub>Ni phase as well as the presence of higher density of embedded MgNi<sub>2</sub> particles in the Fritsch powder which can act as catalysts for hydrogen sorption, differences in the contamination from Fe pick up and MgO impurities content during milling in both powders, difference in the expansion of unit cell volume and mill-dependent different deformation mechanisms of powder particles (e.g. twinning vs. dislocation accumulation).

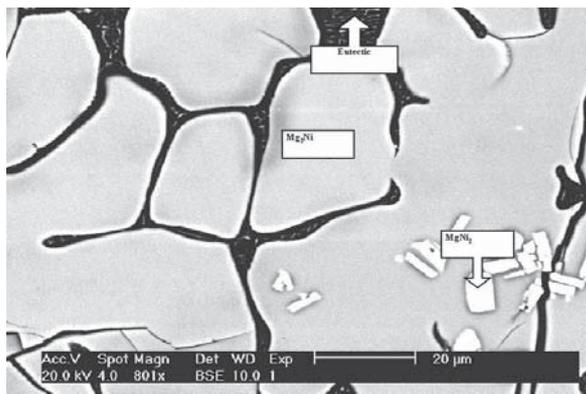
## 1. INTRODUCTION

Hydrogen storage nanocrystalline Mg-Ni alloys are attractive materials for the future development of clean hydrogen energy systems to protect the earth from pollution [1]. The most typical processing techniques to produce the nanocrystalline Mg-Ni powders are mechanical alloying (MA) or mechanical (ball) milling (MM) [2]. The MA process is used to synthesize nanostructured intermetallic or alloying powders starting from elemental metal powders, while the MM is usually applied to fabricate only nanocrystalline powder, for example from pre-alloyed intermetallic ingots [2].

So far, the overwhelming majority of MA or MM processing has been carried out in either planetary (Fritsch) or mixer (Spex) ball mills. The movement of balls in these mills is rather uncontrolled and chaotic. This may be one reason for some conflicting results on the hydriding/dehydriding properties of hydrogen storage nanocrystalline or amorphous powders reported by various research groups in the literature. On the other hand, there is a lack of systematic studies comparing hydriding properties of nanocrystalline powders fabricated by various ball-milling techniques (i.e. types of mills).

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Corresponding author: J. Bystrzycki, e-mail: bystry@wme.wat.edu.pl



**Fig.1.** BSE micrograph of the microstructure of as-solidified ingot (overall composition in at. %: Mg-66.3±0.6; Ni-33.7±0.6).

Recently, Varin *et al.* [3-6] have applied a novel magneto-ball milling technique in a Uni-Ball-Mill 5 to process hydrogen storage Mg-Ni powders in which inefficient chaotic milling is replaced by highly efficient modes based on carefully controlled ball movement by varying both the intensity and/or the direction of magnetic field. The magneto-mill Uni-Ball-Mill 5 utilizes high-field FeNdB permanent magnets to produce an adjustable external field. It has been shown that microstructural evolution in milled Mg-Ni powders is depended on the milling mode under pure shearing (low-and high-energy), impact and mixed conditions. It is suspected that the mode of ball milling can also have a profound effect on the hydrogen sorption properties of Mg-Ni alloys.

Therefore, the objective of the present study was to compare hydriding properties of nanocrystalline powders fabricated in typical, commonly used standard ball mills, such as planetary (Fritsch) and mixer (Spex) ball mills. The first one can be considered as a mill working under mixed shearing-impact mode. However, the second one is a typical ball mill working under strong impact mode.

## 2. EXPERIMENTAL

An ingot of Mg-Ni alloy with the target composition of ~ 33 at. % Ni (bal. Mg) (close to the line intermetallic compound  $Mg_2Ni$ ) was induction melted from pure elements, Mg (99.9%) and Ni (99.9%), under a high-purity argon atmosphere and solidified in the crucible inside the induction furnace. An ingot alloy exhibits a triple-phase microstructure comprising  $Mg_2Ni$ ,  $MgNi_2$  and Mg+ $Mg_2Ni$  eutectic (Fig. 1). At that alloy composition the Mg+ $Mg_2Ni$  eutectic is a non-equilibrium constituent according to the binary

Mg-Ni phase diagram. However, the formation of small amount of Mg+ $Mg_2Ni$  eutectic during solidification is probably a persistent feature of induction melted (IM) Mg-Ni alloys with Ni concentration above 33 at. %. The same behavior was observed by Varin and coworkers [4] in the IM Mg-Ni alloys with Ni>33 at. %

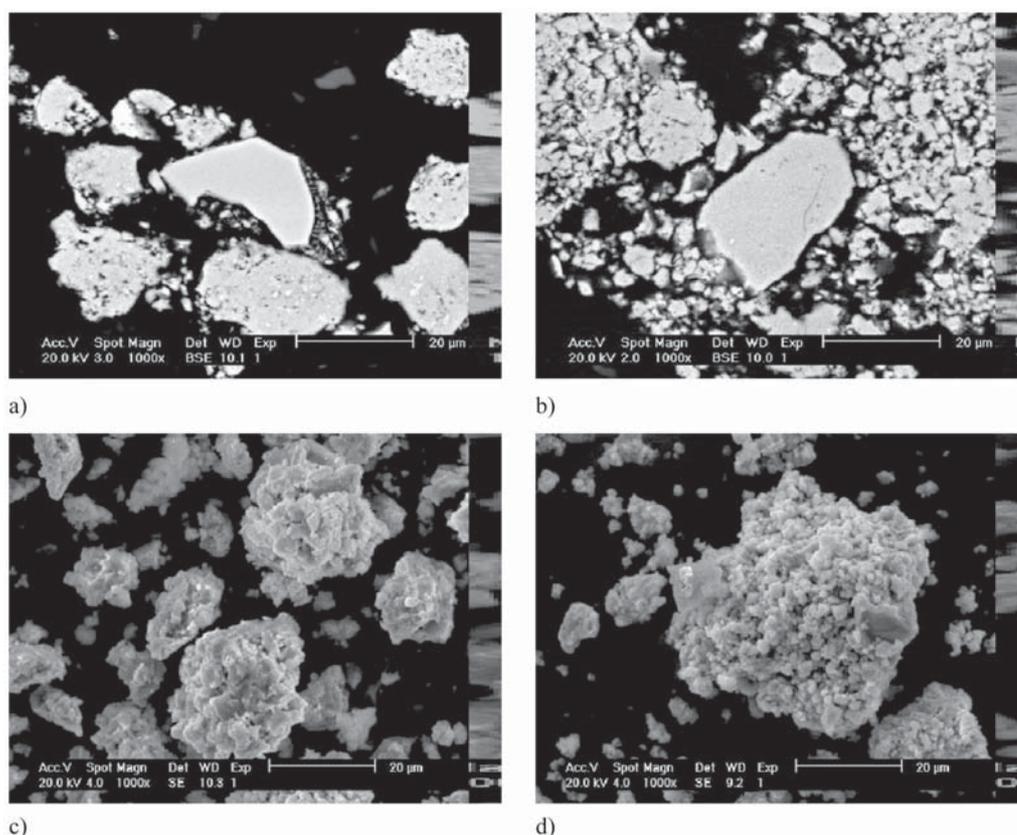
The ingot was mechanically pulverized into coarse powder and subsequently subjected to mechanical ball milling in the argon gas atmosphere (300 kPa) by using a planetary (Fritsch Pullverisette P-5) and a shaker (Spex 8000) ball mills. The milling speed in the planetary mill was 250 rpm. The milling time for both those milling processes was 20 h. It was found in our earlier study [7] that this milling time is sufficient for the formation of nanostructure in the investigated  $Mg_2Ni$ -based powder. The ball-to-powder weight ratio for both processes was 10:1. All powder handlings were performed in a glove bag under high purity argon.

The structure and phase analysis were performed by X-ray diffraction (XRD) using a Seifert X-ray diffractometer at 30 mA, 50 kV and 0.02°/5s step size using  $CuK_{\alpha}$  radiation. The crystallite (nanograin) size was roughly estimated from the well-known Scherrer formula. The morphology and chemical composition of all powders were investigated by scanning electron microscopy (SEM) using a Philips XL30 (LaB6) equipped with automatic image analyzer, backscatter electron detector (BSE) and energy dispersive X-ray spectroscopy (EDAX system).

The hydriding properties of the milled powders were evaluated by volumetric method using an automated Sieverts apparatus at 300 °C under 15 bar hydrogen pressure.

## 3. RESULTS AND DISCUSSION

Fig. 2 shows the microstructure (a,b) and the morphology (c,d) of the milled powders of  $Mg_2Ni$ -based alloy after 20h of ball milling in a planetary (a,c) and a mixer (b,d) ball mills. There is no major difference between the microstructure of both milled powders, which is rather homogeneous and comprises  $Mg_2Ni$  matrix (grey phase) with the embedded  $MgNi_2$  particles (bright specks). It seems, however, that the powder particles obtained from milling in Spex mill exhibit less density of the bright specks at their cross-sections (compare Fig. 2a and 2b) indicating the presence of smaller number of embedded  $MgNi_2$  particles. There is also presence of unreacted Mg+ $Mg_2Ni$  eutectic, which appears as very fine particles (dark phase). SEM observations revealed that



**Fig. 2.** Backscattered electron (BSE) micrographs of the microstructure (a,b) and secondary electron (SE) micrographs of the morphology (c,d) of the  $Mg_2Ni$ -based powder particles processed by milling for 20 h in (a,c) a planetary (Fritsch) ball mill and (b,d) a mixer (Spex) ball mill.

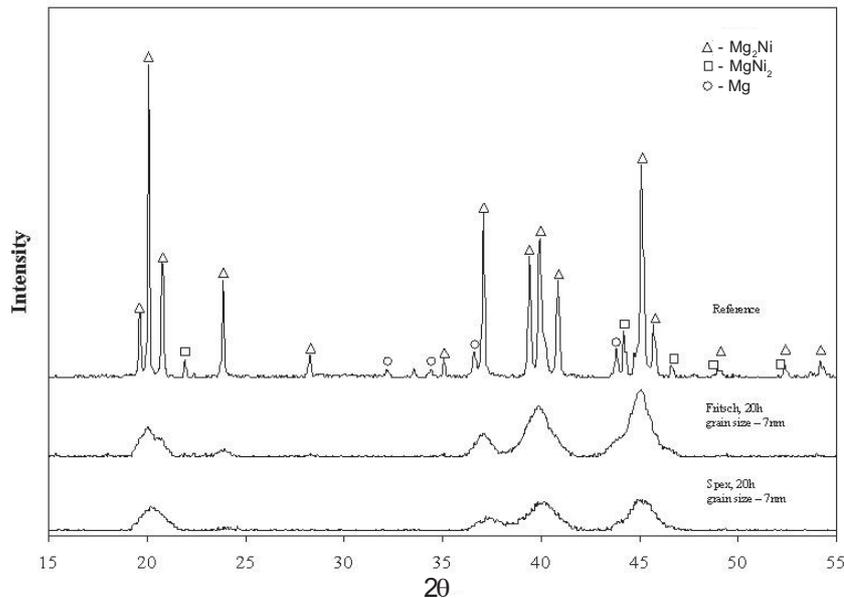
the average particle size decreases from 100-200 to 1-30  $\mu m$  after milling for 20 h in both ball mills.

After milling the particles have a 'popcorn ball' morphology and an agglomeration of smaller particles occurs (Fig. 2c,d). The agglomerated particles possess a porous structure and are composed of small cold-welded particles less than 5  $\mu m$  in size.

The X-ray diffraction spectra of the milled powders and the reference specimen are shown in Fig. 3. As can be seen, they confirm the presence of small amount of  $MgNi_2$  and Mg. The intensity of the diffraction peaks of all existing phases is reduced and the width of the peaks increases after milling for 20 h leading in effect to severe overlap of some closely spaced peaks. The peak broadening indicates that the average crystallite size of the  $Mg_2Ni$  phase decreases approaching  $\sim 7$  nm after milling for 20h in both types of ball mill as roughly estimated from the Scherrer formula. However, XRD diffraction spectrum from the Spex powder seems to indicate that some selected XRD peaks such as (101) (at  $2\theta=20.785^\circ$ ) and (102) (at  $2\theta=23.855^\circ$ ) for the  $Mg_2Ni$  phase [8] completely disappeared. In XRD spectrum from the Fritsch powder, the same peaks are

weak but still recognizable (Fig. 3). This behavior is consistent with the most recent findings by Varin *et al.* [3-5] who reported a partial amorphization of the  $Mg_2Ni$  phase in a multiphase Mg-Ni alloy ( $Mg_2Ni+MgNi_2+Mg$ ) after milling for up to 100 h under shearing mode in the magneto-mill Uni-Ball-Mill 5. It is possible that under highly energetic mostly impact mode in Spex mill amorphization processes are more pronounced as opposed to Fritsch mill.

Hydriding properties of both powders are shown in Fig. 4. It is quite clearly observed that the Fritsch powder exhibits much faster hydriding kinetics than its Spex counterpart. The overall kinetics of hydrogen sorption for the faster absorbing Fritsch powder seems to be roughly in the same range as reported in the literature since it absorbs about 2.7 wt.% of hydrogen after 1800 s (30 min) (Fig. 4). According to the literature, a nanocrystalline  $Mg_2Ni$  processed by mechanical alloying of Mg and Ni elemental powders, having nanograin size in the range of 10-30 nm within the powder particles, absorbs about 3.0-3.5 wt.% hydrogen within 30-60 minutes at  $300^\circ C$  under 1-2 MPa hydrogen pressure in the first absorption cycle without activation [9,10]. However,



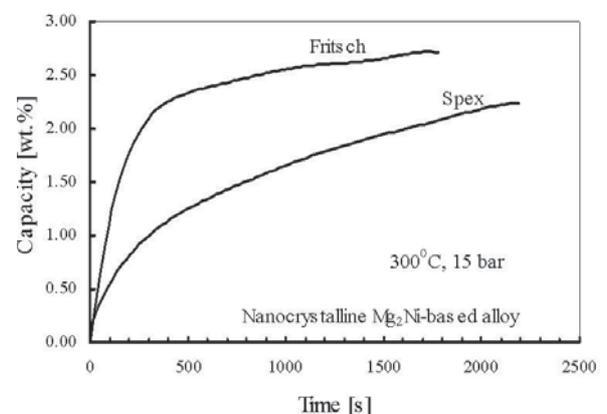
**Fig. 3.** X-ray diffraction (XRD) patterns corresponding to: (a) reference specimen, (b) specimen milled for 20 h in a planetary (Fritsch) ball mill and (c) specimen milled for 20 h in a mixer (Spex) ball mill. The average crystalline size roughly estimated from the Scherrer formula is indicated.

the hydrogen absorption kinetics for the Spex powder in Fig. 4 is more sluggish since it absorbs only ~2 wt.% at the same time of 1800 s. The most plausible explanation of such a difference is that the Spex powder contains more amorphous fraction than the Fritsch powder as discussed above. The gaseous hydrogen capacity of amorphous  $\alpha$ -MgNi alloys processed by mechanical alloying of pre-alloyed  $\text{Mg}_2\text{Ni}$  and elemental Ni has been reported to be in the range of 1.7-2.2 wt.% at the temperature range of 100-200 °C [11,12] which seems to be much smaller than that of nanocrystalline  $\text{Mg}_2\text{Ni}$ . However, some other factors, not investigated yet, should also be taken into account such as the presence of higher density of embedded  $\text{MgNi}_2$  particles in the Fritsch powder which can act as catalysts for hydrogen sorption, difference in the contamination from Fe pick up and MgO impurities content during milling in both powders, difference in the expansion of unit cell volume as recently postulated by Varin and Czujko [13] and different deformation mechanisms of powder particles (e.g. twinning vs. dislocation accumulation).

#### 4. CONCLUSIONS

A nearly single-phase  $\text{Mg}_2\text{Ni}$  alloy obtained by ingot metallurgy was mechanically (ball) milled for 20 h in two types of ball mills: Fritsch and Spex with the objective of obtaining nanocrystalline powders

suitable for subsequent hydrogenation in gaseous hydrogen. Microstructural studies show that regardless of the type of ball mill used the morphology and microstructure is similar in both Fritsch and Spex powders. The average powder particle size is within the range of 1-30  $\mu\text{m}$  and the average nanograin size of the  $\text{Mg}_2\text{Ni}$  phase within the powder particles is on the order of 7 nm as roughly estimated from the Scherrer formula. However, diffrac-



**Fig. 4.** Rate of hydrogen absorption at 300 °C under 15 bar hydrogen pressure by nanocrystalline  $\text{Mg}_2\text{Ni}$ -based powder processed in (a) a planetary (Fritsch) ball mill and (b) a mixer (Spex) ball mill.

tion spectrum from the Spex powder seems to indicate that some selected XRD peaks such as (101) (at  $2\theta=20.785^\circ$ ) and (102) (at  $2\theta=23.855^\circ$ ) for the  $Mg_2Ni$  phase [8] completely disappeared. In XRD spectrum from the Fritsch powder, the same peaks are weak but still recognizable (Fig. 3). The Fritsch powder exhibits much faster hydriding kinetics than its Spex counterpart. The overall kinetics of hydrogen sorption for the faster absorbing Fritsch powder seems to be roughly in the same range as reported in the literature since it absorbs about 2.7 wt.% of hydrogen after 1800 s (30 min). The most plausible explanation of such a difference in the hydriding kinetics between both powders is that the Spex powder contains more amorphous fraction than the Fritsch powder. The hydrogen absorption capacity of the amorphous Mg-Ni fraction is in general lower than that of nanocrystalline fraction.

## ACKNOWLEDGEMENTS

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