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# Characterization of a nanocrystalline Mg–Ni alloy processed by high-pressure torsion during hydrogenation and dehydrogenation

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## ABSTRACT

Ball-milled Mg–Ni powder has been cold-compacted and subsequently processed by severe shear deformation under high-pressure torsion. The effect of high pressure torsion on morphology and microstructure of the disk-shape samples has been characterized by scanning electron microscopy and X-ray diffraction, respectively. In order to achieve partially hydrogenated and dehydrogenated states of deformed samples, the hydrogen uptake or release was interrupted at 25%, 50% and 75% hydrogen contents in a Sieverts' type apparatus. In this paper we present the characterization of the microstructure during a full absorption-desorption cycle of the nanocrystalline Mg–Ni alloy.

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## Introduction

Attempts on effective hydrogen storage have been a key challenge in the last couple of decades [1,2], since hydrogen as an energy carrier can provide significantly more power per mass compared to conventional fossil resources [3]. Albeit it is difficult to increase the hydrogen density above an economical limit in gas state, efficient storage can be achieved in the solid-state by simple and complex metallic hydrides, since they possess remarkable gravimetric and volumetric capacities [4,5]. Elemental magnesium is promising material due to its very high gravimetric capacity (7.6 wt.%), lightweight and

moderate cost, nevertheless the slow  $\text{Mg} \leftrightarrow \text{MgH}_2$  kinetics retards the industrial application of commercial  $\text{MgH}_2$  [6]. Many efforts have been performed to overcome these difficulties, e.g. high energy ball milling (HEBM) has been applied intensively to produce nanocrystalline Mg powders or Mg-based composites [7,8], which can significantly enhance the hydrogenation kinetics due to the abundant grain boundaries and lattice defects [9]. Adding transition metals, like nickel to magnesium by HEBM results in further improved sorption kinetics [10–12]. According to the Mg–Ni binary phase diagram, the two elements are mutually insoluble, whilst two line compounds exist, i.e.  $\text{Mg}_2\text{Ni}$  and  $\text{MgNi}_2$  [13], nevertheless only the former reacts with hydrogen (3.62 wt.%) [14]. By

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applying proper HEBM conditions and concentration, a  $\text{Mg} + \text{Ni} \rightarrow \text{Mg}_2\text{Ni}$  solid-state chemical reaction can take place in the Mg–Ni system [15,16].

Despite the great benefits of HEBM, scaling-up to industrial level of the H-absorbing material production is expensive, which can be achieved by other bulk processing techniques based on severe plastic deformation [17], such as equal-channel angular pressing [18,19], cold rolling [20,21], accumulative roll-bonding [22] and high-pressure torsion (HPT). It was demonstrated that the extreme shear deformation occurring during torsion straining in a HPT device is capable to promote hydrogen uptake in the normally non-absorbing  $\text{MgNi}_2$  phase [23]. When pure bulk Mg is torqued by HPT, the hydrogenation improves significantly [24]. In a recent work we have pointed out that, besides the nanometric crystallite size, dislocations generated during HPT have an important role in the increased amount of absorbed hydrogen in a Mg–Ni alloy [25]. Besides dislocations, stacking faults also positively affect the kinetics of  $\text{Mg}_2\text{Ni}$  processed by HPT [26].

In the present paper, we demonstrate the evolution of the microstructure during hydrogen absorption and desorption of a Mg–Ni alloy processed by HEBM and subsequent HPT. Some of the results are compared to those of a HEBM-processed powder of the same composition.

## Experimental

### Sample preparation

HEBM of commercial polycrystalline Mg and Ni powder blends (supplied by Sigma–Aldrich; purity 99.9%) was carried out in a SPEX 8000 Mixer Mill. The nominal composition of the mixture was  $\text{Mg}_{75}\text{Ni}_{25}$ . Milling time of 10 h ensures the formation of nanocrystalline  $\text{Mg}_2\text{Ni}$  powder through the  $2\text{Mg} + \text{Ni} \rightarrow \text{Mg}_2\text{Ni}$  solid state reaction. Details of the milling conditions are found elsewhere [15]. For subsequent HPT processing, the milled  $\text{Mg}_2\text{Ni}$  powders were cold-compacted into pellets with a diameter of 8 mm and height of 0.8 mm under 1 GPa of hydraulic pressure. High pressure torsion of the pre-compacted pellets was performed under air at room temperature under an applied pressure of 4 GPa and simultaneously shear strain was imposed through  $N = 5$  whole revolutions with an angular speed of  $\omega = 0.2$  revolution/min. In the applied setup the stainless steel anvils obey a constrained geometry [17]. The final thickness of the strained disks is about  $L = 400 \mu\text{m}$ . The accumulated shear strain for torsion deformation at a radius  $r$  can be represented by

$$\epsilon(r, t) = 2\pi \frac{N \cdot r}{L}$$

At the perimeter of our disk-shape samples  $\epsilon(R) \approx 300$ .

### Preparation of partial hydrogenated states

Kinetics of hydrogen release and uptake of the Mg–Ni HPT disks have been carried out in a home-made Sieverts' type apparatus. All measurements were carried out at 300 °C. During absorption the starting pressure was set to 10 bar, while desorption was measured at 0.1 bar. Before each

measurement two full absorption/desorption cycles have been conducted to activate the sample and to determine the reversible hydrogen storage capacity. These hydrogenation and dehydrogenation curves are presented in Fig. 1a and b, respectively. To achieve partially hydrogenated or dehydrogenated states of the HPT samples, the hydrogen uptake and subsequent release was stopped at different hydrogen contents. In order to interrupt the H-sorption reaction, the samples were quenched from 300 °C to room temperature at the desired H-content. During absorption as well as during desorption, states with hydrogen content of 25%, 50% and 75% of the reversible hydrogen capacity were performed, as denoted by gray circles in Fig. 1a and b. Hereafter these states will be denoted as 25%-abs, 50%-abs, 75%-abs, 75%-des, 50%-des and 25%-des. For comparison, fully hydrogenated (100%-abs) and fully dehydrogenated (0%-abs) states were also obtained. It is noted that each state was achieved by using a new HPT-disk.

### Microstructural characterization

Morphology studies were performed on a FEI QUANTA 3D dual beam scanning electron microscope (SEM). The compositional fluctuations have been detected in the back-scattered electron (BSE) mode. For cross-sectional microstructural investigations the disks were embedded in an epoxy resin and mechanically polished to mirror-like surface.

The surface microstructure of the HPT disk was monitored by x-ray powder diffraction (XRD) with  $\text{Cu-K}\alpha$  radiation on a Philips X'pert powder diffractometer in  $\theta$ – $2\theta$  geometry. The instrumental pattern was measured on a NIST SRM660a  $\text{LaB}_6$  peak profile standard material. The average crystallite size ( $D$ ) of the different phases has been determined by applying the Williamson–Hall technique [27] after deconvolution and fitting the Bragg-peaks by pseudo-Voigt function. The typical error of  $D$  is about 10%.

## Results and discussion

### Characterization of the HEBM powder and the HPT-disk

The XRD pattern of the HEBM 10 h powder sample is dominated by the diffraction peaks of hexagonal  $\text{Mg}_2\text{Ni}$  intermetallic compound (JCPDS 35–1225;  $a = 5.21 \text{ \AA}$ ;  $c = 13.323 \text{ \AA}$ ) with some traces of unreacted Ni (Fig. 2). Although the as-received powder contains excess Mg compared to the stoichiometric concentration, the presence of residual Ni is associated with different mechanical properties of the two components [15,20]. The excess Mg probably forms an amorphous phase with a low volume fraction and/or covers the inner surfaces of the milling vial which cannot be detected by XRD [28]. In a very recent paper Hou et al. demonstrated that the proper choice of the ball to powder mass ration can eliminate the unreacted nickel in the Mg–Ni system [29]. As it is noticed, some traces of  $\text{MgO}$  are also present. The obtained average size of the  $\text{Mg}_2\text{Ni}$  crystallites is in the nanometric range ( $\sim 8 \text{ nm}$ ), see Fig. 3. Secondary electron SEM image of the HEBM 10 h powder sample presents that individual powder particles exhibit sharp edges which are a consequence of ball milling (Fig. 4a).

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