




## Article

# Synthesis of Nanostructured $\text{Mg}_2\text{Ni}$ for Hydrogen Storage by Mechanical Alloying via High-Pressure Torsion

Edgar Ignacio López Gómez <sup>1,2,\*</sup> , Joaquín Gonzalez <sup>2</sup>, Jorge M. Cubero-Sesin <sup>2</sup>  and Jacques Huot <sup>1,\*</sup> 

<sup>1</sup> Hydrogen Research Institute, Université du Québec à Trois-Rivières, 3351 Boul. des Forges, Trois-Rivières, Québec, QC G9A 5H7, Canada

<sup>2</sup> Centro de Investigación y Extensión en Materiales (CIEMTEC), Escuela de Ciencia e Ingeniería de los Materiales, Instituto Tecnológico de Costa Rica (ITCR), Cartago 159-7050, Costa Rica; jegonzalez@tec.ac.cr (J.G.); jcubero@itcr.ac.cr (J.M.C.-S.)

\* Correspondence: edgar.ignacio.lopez.gomez@uqtr.ca (E.I.L.G.); jacques.huot@uqtr.ca (J.H.)

**Abstract:**  $\text{Mg}_2\text{Ni}$  is a highly promising candidate for solid-state hydrogen storage due to its high storage capacity. However, its synthesis is challenging due to the high melting point of Ni (1455 °C) and the boiling point of Mg (1090 °C). In this study, elemental powder mixtures of Mg and 30 at% Ni were processed by high-pressure torsion (HPT) to synthesize the  $\text{Mg}_2\text{Ni}$  intermetallic compound through mechanical methods. The formation of 11 wt% of  $\text{Mg}_2\text{Ni}$  after 50 turns of HPT was confirmed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS), reaching a maximum of 59 wt% after 100 turns. Rietveld refinement confirmed a nanocrystalline size for the  $\text{Mg}_2\text{Ni}$  phase synthesized via HPT. Hydrogenation tests showed that the Mg-Ni synthesized by HPT can absorb hydrogen at 350 °C even after several weeks of air exposure. Furthermore, a maximum absorption capacity of 3.8 wt% was reached after 20 h of hydrogen exposure for the sample with 100 turns. This capacity is close to the theoretical capacity of 3.9 wt% for this composition. The results confirm that combining HPT with subsequent heat treatment is an efficient strategy to increase the  $\text{Mg}_2\text{Ni}$  fraction after HPT processing.

**Keywords:** severe plastic deformation (SPD); hydrogen storage; metal hydrides; magnesium–nickel intermetallics; nanostructured alloys



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## 1. Introduction

It is widely recognized that hydrogen serves as an excellent clean energy carrier and has the potential to be utilized in both stationary and mobile applications [1–3]. Hydrogen possesses a gravimetric energy density over three times higher than common hydrocarbon fuels [3]. Nevertheless, various technical aspects of hydrogen storage materials and systems constrain industrial applications. Nowadays, methods involving gas or cryogenic liquid states are commonly utilized for hydrogen storage [1–3]. For instance, hydrogen-powered vehicles utilize high-pressure gas stored at 70 MPa [2,4]. However, the high cost and volume of these tanks limit their application in fields with higher energy demands [1–3].

Solid-state systems using metal hydrides is another safe means of hydrogen storage. Theoretically, pure Mg can absorb 7.6 wt% H, pure Al can absorb 11 wt% H, and alloys such as  $\text{LaNi}_5$  and TiFe can absorb 1.5 wt% and 1.8 wt% H, respectively. However, the thermodynamic properties of metal hydrides are one of the main factors that prevent the adoption of solid-state systems [5–13]. Mg is one of the most promising elements due to its relatively high storage capacity and low weight. Unfortunately, a high desorption temperature makes its implementation as a hydrogen storage material difficult. Therefore, the development of new materials that will store hydrogen in a solid state is vital for the widespread application of hydrogen as a clean energy carrier at the industrial level.

Different methods have been applied to modify the hydrogen storage properties of metal hydrides. Chemical modification by alloying, i.e., Mg-Ni and Ti-Fe alloys, cata-

lysts such Zr and oxides ( $\text{Nb}_2\text{O}_5$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{TiO}_2$ ) [14–22], solid solutions (Ti–Cr–Fe, TiFe–O) [14,23], and other methods have demonstrated positive effects in modifying the hydrogenation properties of pure metals [11,24]. In the Mg–Ni system, the  $\text{Mg}_2\text{Ni}$  intermetallic phase shows good properties for solid-state hydrogen storage, with a theoretical gravimetric capacity of 3.8 wt% H.

However, the synthesis process of  $\text{Mg}_2\text{Ni}$  and Mg–Ni alloys is a complicated procedure using common metallurgical methods, mainly due to the low boiling point of Mg (1090 °C) and the high melting point of Ni (1455 °C). In addition, the phase diagram Mg–Ni involves a peritectic and a eutectic reaction taking place subsequently during the cooling process [25]; therefore, products such as  $\text{MgNi}_2$  are also produced, reducing the yield and the hydrogen storage capacity.

To limit this temperature gap, different researchers have shown the effectiveness of mechanical alloying processes such ball milling [26–33] and cold rolling [34,35], with good results in the synthesis of  $\text{Mg}_2\text{Ni}$  and other compounds. Emami et al. processed powder mixtures of Mg–33 at% X by HPT, with X corresponding to 21 different elements including Ni [36]. Emami et al. reported the synthesis of  $\text{Mg}_{17}\text{Al}_{12}$ ,  $\text{MgZn}$ ,  $\text{MgAg}$ ,  $\text{Mg}_2\text{In}$ , and  $\text{Mg}_2\text{Sn}$  under a pressure of 3 GPa for 100 turns. They reported a phase transformation to  $\text{Mg}_2\text{Ni}$  just after an HT post-HPT. Additionally, the intermetallic compound TiFe has previously been synthesized after 10 turns [37]. Other immiscible systems such as Mg–Zr [38], Mg–Ti [39], and Mg–Hf [40] has also previously been synthesized by HPT.

Severe plastic deformation (SPD) methods, such as HPT [41–43] and equal-channel angular processing (ECAP) [44–48], have been used due to their capacity to achieve high strain and grain refinement even in metals with high hardness. SPD has also been shown to produce fast hydrogen transport on casted intermetallics due to the high density of grain boundaries and crystalline defects, also enhancing the activation and hydrogenation kinetics [36,49–59].

Mechanical processing has also shown good results in the thermal activation of TiFe and in the kinetics of absorption via the effect of grain refinement [11]. In Mg alloys, the effect of grain refinement shows improvements in the kinetics of absorption [11,26,28,32,60]. Hongo et al. reported the formation of nanograins and stacking faults in  $\text{Mg}_2\text{Ni}$  ingots processed by HPT, with a high hydrogen capacity (3.3 wt% H at 150 °C) and improved absorption kinetics with respect to the annealed ingot material [58]. Edalati et al. also synthesized homogeneous  $\text{Mg}_4\text{NiPd}$  alloy with a bcc structure and low hydrogen binding energy by using the HPT process for 1500 turns. This alloy reversibly absorbed and desorbed 0.7 wt% H at 32 °C [59]. However, previous HPT studies do not show any evidence of the synthesis of  $\text{Mg}_2\text{Ni}$  from the binary powder mixture as in ball milling [26–33] and cold rolling [34].

In this work, we systematically studied the synthesis of nanocrystalline  $\text{Mg}_2\text{Ni}$  using the HPT process under higher pressures of up to 6 GPa, starting from a binary elemental powder mixture close to the stoichiometric composition. The main advantages of the HPT method in contrast to the ball milling technique are the absence of an inert atmosphere [34], the reduction in contamination during the process [61,62], and the absence of a reactive powder after milling. The microstructure, crystal structure, and hydrogen storage properties of materials were investigated.

## 2. Materials and Methods

### 2.1. Materials

High-purity Mg powder (99.8%) from Thermo Scientific Chemicals (Waltham, MA USA), with a particle size below 250  $\mu\text{m}$ , was mixed with 30 at% of high-purity Ni (99.99%) from Millipore Sigma Canada Ltd (Oakville, ON, Canada), with a particle size below 150  $\mu\text{m}$ . The powders were mixed by manual stirring for 3 min and by ultrasonic bathing in acetone for 7 min; this was repeated for 30 min. Then, the acetone was evaporated completely. The powder mixture was pre-compacted into a disc shape of 10 mm diameter in a manual hydraulic press.

## 2.2. HPT Procedure and Equipment

The pre-compacted discs were processed by HPT under 6 GPa of pressure at ambient temperature for 3, 10, 20, 40, 50, 88, and 100 turns (now referred to as N3, N10, N20, N50, N40, N88, and N100 samples, respectively) with a rotation speed of 1 rpm. The powders and the samples were processed and manipulated in an air atmosphere. The  $\gamma$  induced in HPT can be considered as the shear strain described in Equation (1), where  $r$  is the distance from the center of the disc,  $N$  is the number of turns during the HPT, and  $h$  is the thickness of the disc [63].

$$\gamma = \frac{2\pi r N}{h} \quad (1)$$

A custom HPT equipment consisting of a four-column hydraulic press with a capacity of 200 tons (YH32-200 XZPRESTTEK) and a electromechanical torsion machine (SISELEC SA, San José, Costa Rica) was used. The discs were placed between two anvils of D2 tool steel in the torsion system, each with a cavity of 10 mm diameter and 0.5 mm depth for the sample processing.

## 2.3. Characterization Methods

The samples were examined by XRD using a Bruker Focus D8 diffractometer with Cu K $\alpha$  radiation. Rietveld analysis using TOPAS [64,65] was carried out to quantify the phase composition. The samples were also examined by SEM using a Hitachi SU1510 instrument equipped with an Oxford Instruments X-Max EDS to evaluate the microstructural evolution and the chemical composition. The hydrogen storage performance was measured using a homemade Sieverts apparatus at 350 °C under a hydrogen pressure of 2000 kPa.

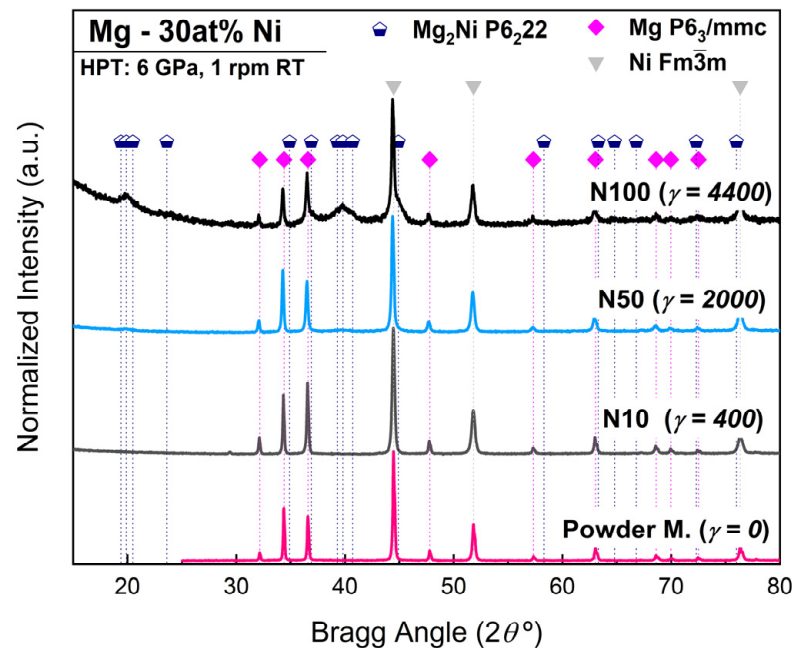
## 3. Results and Discussion

### 3.1. Synthesis and Characterization of Mg<sub>2</sub>Ni by HPT

The phase formation and the microstructural evolution in the Mg-Ni mixtures after HPT were examined by XRD at different numbers of turns. The XRD pattern given in Figure 1 shows the results taken near the edge of the discs for the samples with 10, 50, and 100 turns. After 10 turns, slight variations can be observed in the diffraction pattern of Mg and Ni phases in comparison to the powder mixture. Peak broadening was observed in the Ni phase, which gave a crystallite size reduction to 82 nm, while Mg showed mainly only changes in the intensities of diffracting planes, with a crystallite size of 163 nm. Table 1 summarizes the phase composition and lattice parameters of the powder mixture, and the HPT samples processed by 10, 50, and 100 turns. According to the XRD results in Table 1, Mg and Ni do not show a large change in their crystal size from 10 to 50 turns. Further processing after 100 turns shows a crystallite size reduction in Mg and Ni to 70  $\mu$ m and 57  $\mu$ m, respectively.

The XRD pattern given in Figure 1 clearly shows new broad peaks appearing after 100 turns, which are centered at  $\sim 19.8^\circ$  and  $\sim 39.8^\circ$ , suggesting the growth of a new nanocrystalline phase. According to the XRD analysis and Rietveld refinement results, it was possible to identify that these peaks fit well to the Bragg peaks of Mg<sub>2</sub>Ni with hcp structure P6<sub>2</sub>22. After 100 turns, 59 wt% of the Mg<sub>2</sub>Ni phase was identified, with a crystallite size of 6 nm. Furthermore, even after 50 turns, it was possible to identify 11 wt% of the Mg<sub>2</sub>Ni phase.

The formation of the Mg<sub>2</sub>Ni phase was also analyzed by XRD in different regions of the HPT disc processed for 100 turns. In addition to the edge scan, the disc sample was scanned at the center, both at the upper and lower surfaces (where  $\gamma$  is lower, theoretically in a region corresponding to strains from 0 to 3100), according to Equation (1). Figure 2 shows the XRD pattern results of Mg-30 at% Ni processed for 100 turns in the aforementioned disc regions and corresponding strain levels, while Table 2 shows the phase composition and lattice parameters of the resulting phases.

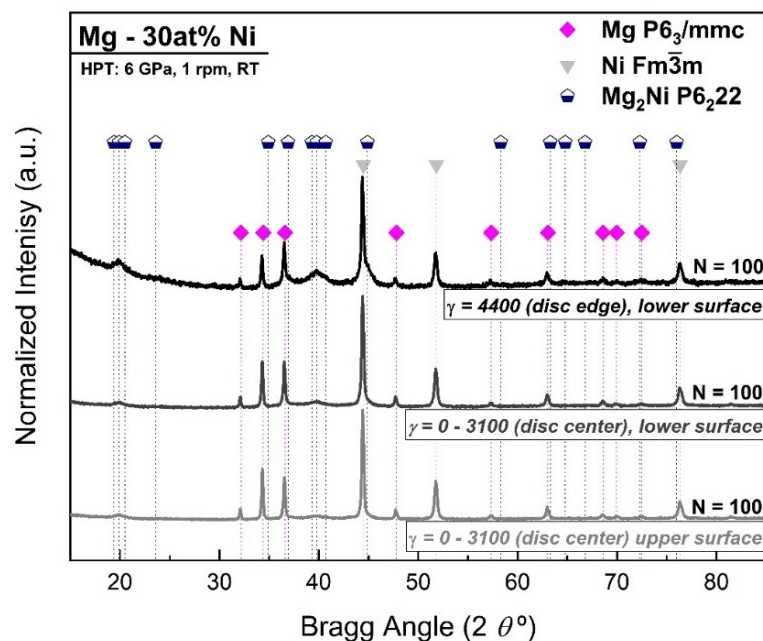


**Figure 1.** XRD patterns of Mg-Ni initial powder mixture and after HPT processing for 10, 50, and 100 turns showing gradual formation of nanostructured  $\text{Mg}_2\text{Ni}$  by HPT.

**Table 1.** Crystallographic parameters of phases present in Mg-30 at% Ni powder mixture and processed by 10, 50, and 100 turns of HPT.

Condition	Phase	wt%	a (Å)	c (Å)	Crystallite Size (nm)
Powder Mixture	Mg hcp	46 (3)	3.2102 (3)	5.2118 (1)	-
	Ni fcc	54 (5)	3.5251 (2)	-	-
HPT N10 $\gamma = 400$	Mg hcp	44 (3)	3.2104 (1)	5.2125 (2)	163 (7)
	Ni fcc	56 (3)	3.5252 (1)	-	82 (2)
HPT N50 $\gamma = 2000$	Mg hcp	42 (2)	3.2101 (2)	5.2110 (3)	168 (2)
	Ni fcc	47 (3)	3.5246 (1)	-	80 (2)
	$\text{Mg}_2\text{Ni}$ hcp	11 (2)	5.27 (1)	13.35 (6)	6 (1)
HPT N100 $\gamma = 4400$	Mg hcp	18 (2)	3.2099 (4)	5.2129 (6)	70 (3)
	Ni fcc	24 (3)	3.5249 (3)	-	57 (1)
	$\text{Mg}_2\text{Ni}$ hcp	59 (3)	5.230 (2)	13.30 (1)	6 (1)

The XRD patterns in Figure 2 and Rietveld refinement results in Table 2 show that the  $\text{Mg}_2\text{Ni}$  phase clearly increased from the upper (21 wt%) to the lower surface (30 wt%). Such differences across the thickness of the disc could happen as result of slippage between the sample and anvils, especially at a high number of turns [66]. Also, in comparison with the results in Table 1,  $\text{Mg}_2\text{Ni}$  reaches a maximum of 59 wt% at the edge of the disc after HPT processing, where the strain reaches the maximum in the radial direction ( $\gamma = 4400$ ). Also, for the Mg and Ni phases, the crystallite size decreases at the edge of the sample where the shear strain is highest. Rietveld refinement confirms a crystallite size of less than 6 nm for the  $\text{Mg}_2\text{Ni}$  hcp phase, which is in good agreement with previous HPT processes, where Mg-Ti [39], Mg-Zr [38], and Mg-based immiscible systems were also synthesized [41,58,59,67].



**Figure 2.** XRD patterns of Mg-30 at% Ni at upper surface ( $\gamma = 0$  by theory), lower surface ( $\gamma = 3100$ ), and edge of the disc ( $\gamma = 4400$ ) showing the formation of nanostructured  $\text{Mg}_2\text{Ni}$  when the strain by HPT increases.

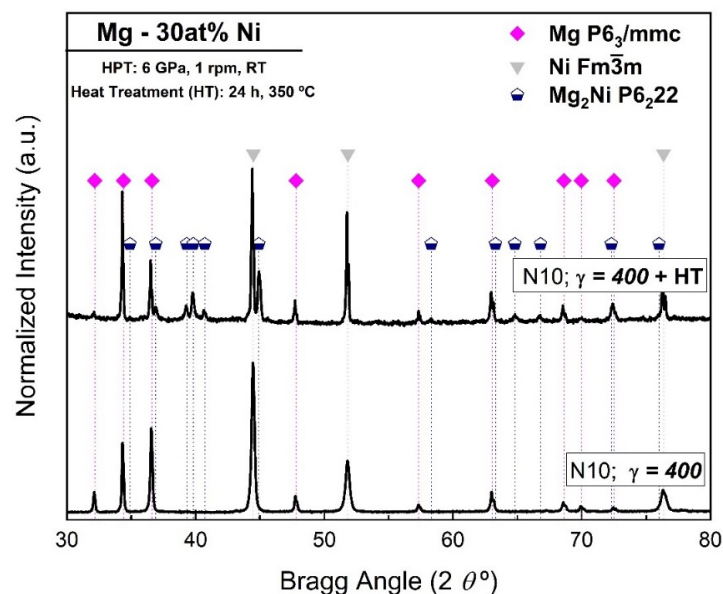
**Table 2.** Crystallographic parameters of phases present in Mg-30 at% Ni processed by HPT for 100 turns.

Condition	Phase	wt%	a (Å)	c (Å)	Crystallite Size (nm)
HPT N100	Mg hcp	34 (2)	3.2124 (2)	5.2148 (3)	156 (11)
$\gamma = 0-3100$	Ni fcc	44 (3)	3.5267 (1)	-	89 (2)
Upper surface	$\text{Mg}_2\text{Ni}$ hcp	21 (2)	5.252 (5)	13.35 (3)	6 (3)
HPT N100	Mg hcp	31 (2)	3.2108 (2)	5.2119 (3)	121 (7)
$\gamma = 0-3100$	Ni fcc	39 (2)	3.5258 (2)	-	76 (6)
Lower surface	$\text{Mg}_2\text{Ni}$ hcp	30 (2)	5.248 (6)	13.39 (3)	5 (2)

The effect of an HT was also studied for the Mg-30 at% Ni processed by 10 turns of HPT. Figure 3 shows the results for Mg-30 at% Ni after 10 turns, with (N10,  $\gamma = 400 + \text{HT}$ ) and without HT (N10,  $\gamma = 400$ ). In Figure 3, it is possible to observe that after the HT, the peaks belonging to  $\text{Mg}_2\text{Ni}$  can clearly be seen and correspond to 34 wt%, as shown in Table 3.

These results confirm that even when the  $\text{Mg}_2\text{Ni}$  phase was not observed in the sample after 10 turns, the HT post-HPT enhanced the formation of the  $\text{Mg}_2\text{Ni}$  phase. This is consistent with the work of Emami et al. [36]. The results also show grain growth in the Ni and Mg phases after the HT. The Ni phase crystallite size increased from 82 nm to 146 nm, while the Mg phase increased from 163 nm to a size too large to be accurately measured by XRD. The Rietveld results also show that after the HT, the crystallite size of the  $\text{Mg}_2\text{Ni}$  phase remains at a nano size (85 nm) and Ni remains at an ultra-fine size (146 nm). Regarding the XRD analysis in Figures 1–3 and Tables 1–3, there is no evidence of oxide formation after the HPT process or after the HT, at least under the detection limit of the XRD technique.



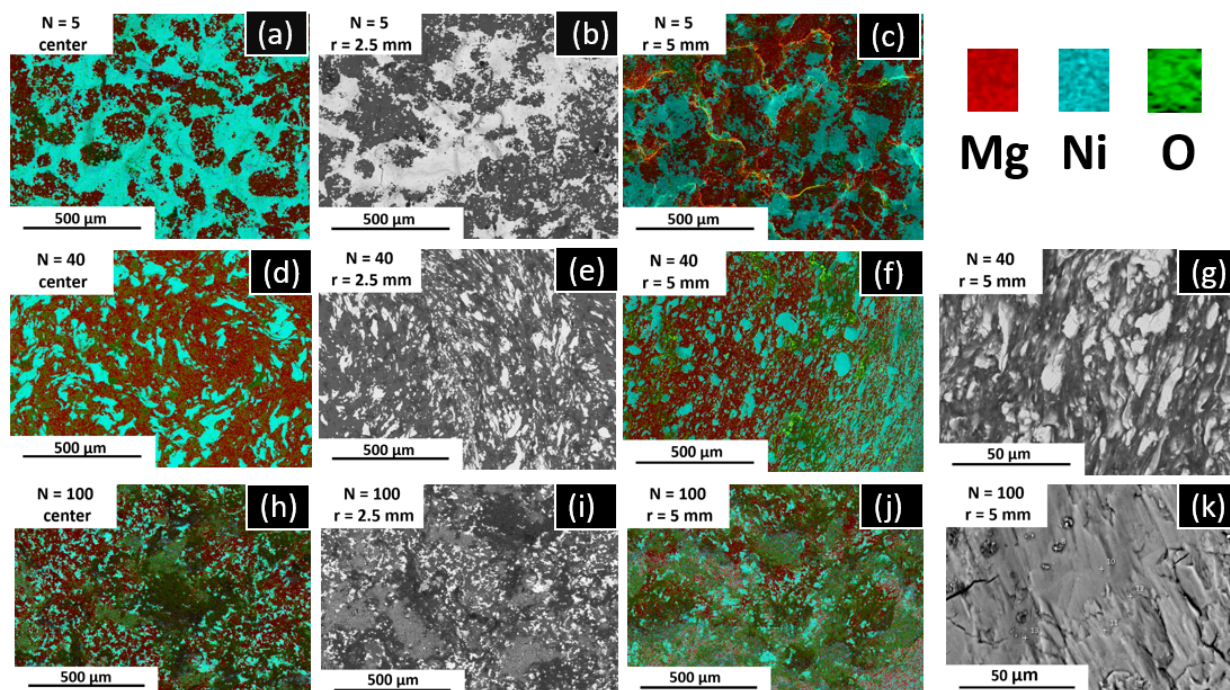


**Figure 3.** XRD patterns of Mg-30 at% Ni processed by HPT for 10 turns ( $\gamma = 400$ ) with and without heat treatment.

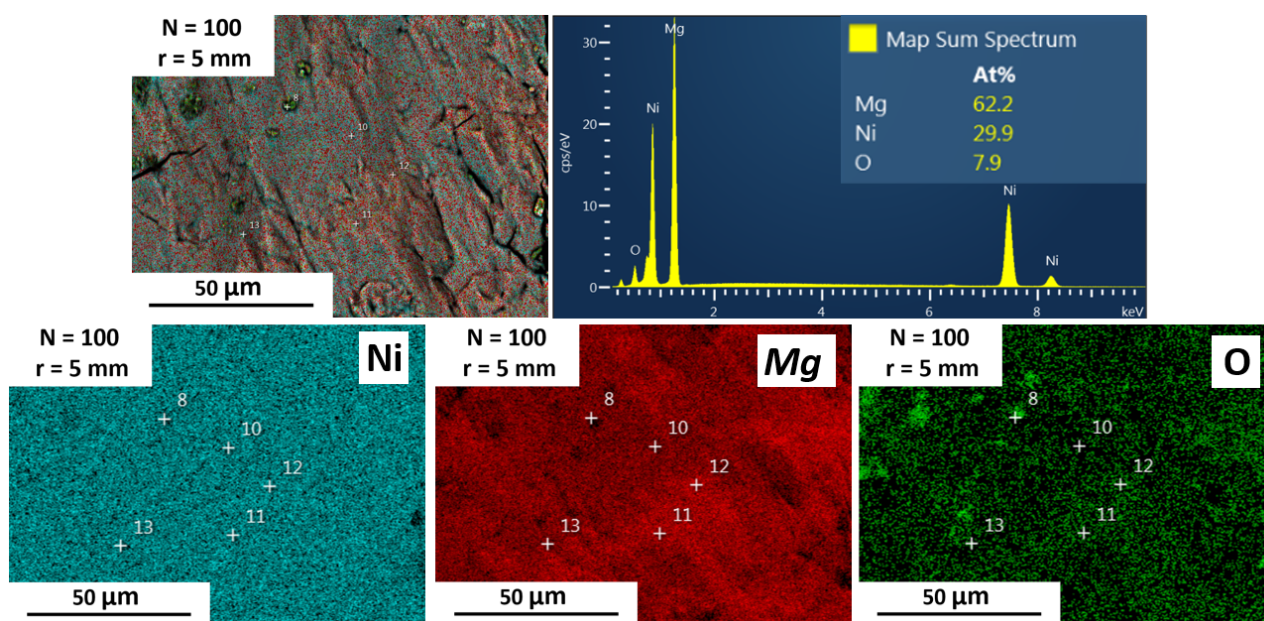
**Table 3.** Crystallographic parameters of phases present in Mg-30 at% Ni processed by HPT for 10 turns ( $\gamma = 400$ ) after heat treatment at 350 °C for 24 h.

Condition	Phase	wt%	a (Å)	c (Å)	Crystallite Size (nm)
HPT N10	Mg hcp	33 (2)	3.2110 (2)	5.2106 (2)	-
$\gamma = 400$	Ni fcc	33 (2)	3.5251 (1)	-	146 (7)
HT 350 °C	Mg <sub>2</sub> Ni hcp	34 (2)	5.2196 (3)	13.2713 (18)	85 (5)

SEM-EDS was performed at different distances from the center of the disc, to analyze at the micrometer level the elemental distribution of Mg and Ni and the degree of mixing. Figure 4 shows the results for Mg-30 at% Ni processed after 5 (Figure 4a–c), 40 (Figure 4d–g), and 100 (Figure 4h–k) turns. After five turns (Figure 4a–c), the images reveal that Mg and Ni are completely separated from each other, showing dark and bright contrast regions, respectively. The EDS elemental mapping shown in Figure 4a,c confirms this statement. Further HPT processing shows an improvement in the Mg–Ni intermixing, as can be seen in Figure 4d–k. Also, when increasing the number of turns (i.e., from 5 to 40 turns) and increasing the distance from the center of the disc (up to 5 mm), the particle size of Mg and Ni is reduced, improving the mixing of the elements. This behavior is in good agreement with previous reports, where the homogeneity of the elemental powder mixture increases with the increase in the strain for Mg–Al [68], Mg–Zr [38], Al–Fe [69], Cu–Ta [70], Nb–Ti [71], and Ti–Nb [72]. The samples also show a clear torsional shear deformation pattern at the center of the disc after 5 and 40 turns (Figure 4a,d), which becomes less evident after 100 turns (Figure 4h). In general, after 100 turns, a randomly oriented microstructure was developed due to the increment of the homogeneity and the phase transformation to Mg<sub>2</sub>Ni. Figure 4 confirms that there are some spots at the edge of the disc where the complete mixture occurred, showing a single-phase contrast. The EDS elemental mapping analysis in Figure 5 shows a composition ratio of Mg to Ni of ~2 at the edge of the sample (62.2 at% Mg to 29.9 at% Ni). It was also possible to observe that some surface oxides (7.9 at%) were formed after the HPT process, which are mainly over the Mg phase. In addition, the average of spectra 10, 11, 12, and 13 shown in Figure 5 are 63 at% ( $\pm 4$ ), 28 at% ( $\pm 6$ ), and 7 at% ( $\pm 1$ ) of Mg, Ni, and O, respectively. Thus, the experimental composition identified by EDS is consistent with the Mg<sub>2</sub>Ni phase identified by XRD and Rietveld refinement.



**Figure 4.** SEM BSE micrographs (b,e,g,i,k) and EDS elemental mapping analysis (a,c,d,f,h,j) of Mg powder (a) and Mg-30 at% Ni after HPT processing for different numbers of turns, taken from center (left, (a,d,f)), the middle (b,e,i), and the edge of the disc (c,f,g,j,k). Bright and dark contrast in SEM micrographs correspond to Ni and Mg, respectively.

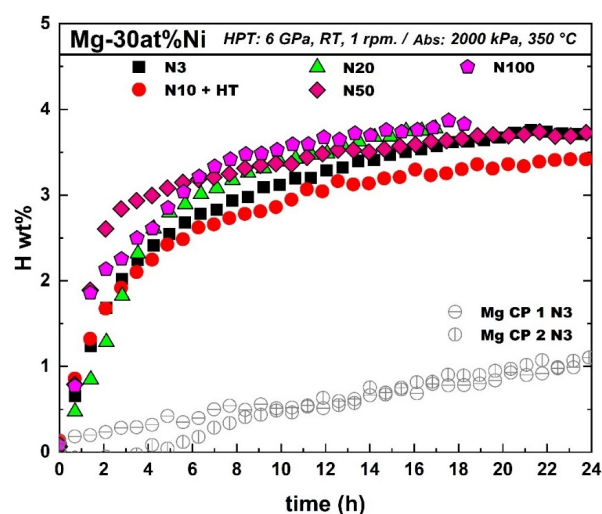


**Figure 5.** EDS mapping analysis of Mg-30 at% Ni processed for 100 turns at the edge of the disc ( $r = 5$  mm,  $\gamma = 4400$ ). The + sign indicated the spots where EDS compositions were recorded.

### 3.2. Hydrogen Storage Properties of Mg-Ni Processed by HPT

Figure 6 shows the hydrogenation kinetics of Mg-30 at% Ni processed with 3, 10, 20, 50, and 100 turns. It should be noted that the hydrogenation tests were performed several weeks after the HPT processing and that the samples were left in the air during the whole period. Therefore, these tests also indicate the air resistance of the HPT-processed samples. Samples with 20 and 100 turns show a maximum capacity of 3.8 wt% of hydrogen at 350 °C

after 18 h, which is close to the nominal capacity of the material (3.9 wt%). Samples with 3 and 50 turns show a lower capacity of 3.7 wt% after 20 h, while the storage capacity of the sample with heat treatment is reduced to 3.4 wt% after 24 h. According to this, the sample N100 optimizes both the synthesizing and storage capacity. The hydrogen storage capacity obtained in this work is higher than the capacity reported for Mg-Ni processed by different severe plastic deformation processes, as shown in Table 4, such as high-energy ball milling (HEBM) (2.4 wt%), HEBM + HPT (3 wt%), casting + HPT (3.3 wt%), HEBM with cold rolling (2.4 wt%), and HEBM + ECAP (1.5 wt%) [44,58,73,74]. Figure 6 also shows the activation results of a commercially pure (CP) Mg process with three turns for comparison purposes. It is clear in Figure 6 that the addition of Ni helps to accelerate the absorption of Mg even just after three turns of HPT.



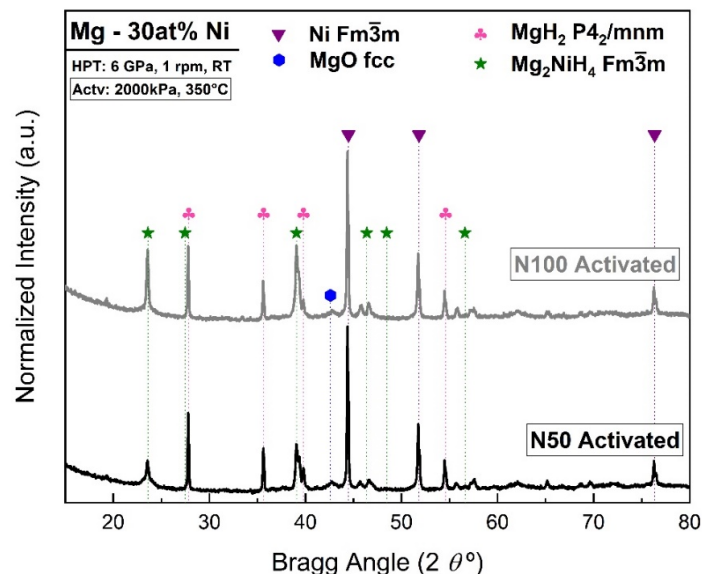
**Figure 6.** Hydrogenation results of commercially pure Mg after 3 turns and Mg-30 at% Ni after 3, 10, 20, 50, and 100 turns of HPT.

**Table 4.** Hydrogen storage of some Mg-Ni systems processed by SPD process.

Sample + Condition	Synthesis Process	SPD Process	Activation	Ref.
Mg <sub>2</sub> Ni/annealing	Casting	-	2.2 wt%, 20 h	[58]
Mg <sub>2</sub> Ni/annealing + HPT	Casting	HPT, 6 GPa, N10	3.3 wt%, 20 h	
Mg <sub>2</sub> Ni/annealing + HPT + annealing	Casting	HPT, 6 GPa, N10	3.3 wt%, 20 h	
Mg-25 at% Ni/HEBM+ HPT	HEBM	HPT, 2 GPa, N5	1.6 wt%, 5 h	[73]
Mg-25 at% Ni/HEBM+ CR4	HEBM 10h	Cold rolling	2.4 wt%, 0.5 h	[44]
Mg-25 at% Ni/HEBM+ CR10	HEBM 10h	Cold rolling	2.4 wt%, 1 h	
Mg-25 at% Ni/HEBM+ ECAP 2x	HEBM 10h	ECAP	1.5 wt%, 0.5 h	
Mg-25 at% Ni/HEBM+ ECAP 6x	HEBM 10h	ECAP	1.5 wt%, 0.5 h	
Mg-30 at% Ni/HEBM	HEBM 1h	-	2 wt%, 0.5 h	[74]
Mg-30 at% Ni/HEBM + HPT	HEBM 1h	HPT, 6 GPa, N5	3 wt%, 1.7 h	
Mg-30 at% Ni/HEBM	HEBM 10h	-	2.4 wt, 0.5 h	
Mg-30 at% Ni/HEBM + HPT	HEBM 10h	HPT, 6 GPa, N5	3 wt%, 1.7 h	
Mg-30 at% Ni/HPT (+60 days in Air)	HPT: 6 GPa, 1 rpm, N= 3–100		3.8 wt%, 18 h	This work

In order to evaluate the hydride formation in the Mg-Ni system, XRD patterns were taken after the hydrogen absorption test. Figure 7 shows the diffraction pattern for the activated Mg-30 at% Ni with 50 and 100 HPT turns. The XRD results confirm the formation of hydride phases after the hydrogenation test for all the samples. Further analysis by Rietveld refinement confirms the formation of MgH<sub>2</sub> and Mg<sub>2</sub>NiH<sub>4</sub> in Mg-30 at% Ni after 100 turns, as shown in Figure 7.





**Figure 7.** XRD patterns showing hydride formation in Mg-30 at% Ni processed by HPT for 50 and 100 turns and activated under 2000 kPa and 350 °C.

Table 5 summarizes the Rietveld refinement results for Mg-30 at% Ni processed by HPT for 50 and 100 turns after first hydrogenation (activation). It can be seen that when increasing from 50 to 100 turns, the amount of  $\text{Mg}_2\text{Ni}$  hydride phase also increases, which means a reduction in the amount of  $\text{MgH}_2$  and Ni phases. A  $\text{MgO}$  phase has also been identified after the activation test; this oxide phase was not identified in the powder mixture before HPT processing by XRD, as shown in Figure 1 and Table 1, which suggests that the oxide phase increases during the manipulation after the activation test, probably due to fresh surface exposed.

**Table 5.** Crystallographic parameters of the phases present after first hydrogenation (activation) of Mg-30 at% Ni processed by HPT.

Condition	Phase	wt%	a (Å)	c (Å)	Crystallite Size (nm)
HPT N50, $\gamma = 2000$ Activated	Ni fcc	25 (1)	3.5252 (1)	-	103 (4)
	$\text{MgH}_2$	23 (1)	4.5181 (3)	3.0224 (3)	127 (18)
	$\text{MgO}$	22 (2)	4.218 (3)	-	5 (1)
	$\text{Mg}_2\text{NiH}_4$	31 (1)	14.614 (4)	b = 6.415 (2), c = 6.494 (3), beta = 115.7 (1)	24 (1)
HPT N100, $\gamma = 4400$ Activated	Ni fcc	22.5 (9)	3.5251 (14)	-	91 (3)
	$\text{MgH}_2$	17.0 (8)	4.5184 (3)	3.0225 (3)	162 (12)
	$\text{MgO}$	23 (2)	4.216 (4)	-	3.2 (3)
	$\text{Mg}_2\text{NiH}_4$	38 (2)	14.6163 (18)	b = 6.426 (4), c = 6.489 (1), beta = 115.9° (1)	40 (1)

#### 4. Conclusions

Mechanical synthesis of  $\text{Mg}_2\text{Ni}$  has been achieved for the first time through HPT processing directly from binary elemental powder mixtures. This study shows that through HPT processing, it is possible to synthesize the intermetallic compound from the powder mixture via a solid-state reaction. The result is in good agreement with previous research where new phase formations of  $\text{Mg}_{17}\text{Al}_{12}$ ,  $\text{MgZn}$ ,  $\text{MgAg}$ ,  $\text{MgIn}$ , and  $\text{Mg}_2\text{Sn}$  were also synthesized by solid-stated reactions under 3 GPa and 100 turns of HPT [36].

It was also found that pressure is an important parameter that affects the phase transformation during HPT and hydrogen storage properties. The present results show

that at 6 GPa, it was possible to detect Mg<sub>2</sub>Ni by XRD after 50 turns without any heat treatment, which was not reported in HPT performed under 3 GPa after 100 turns [36]. The present results confirm a maximum amount of 59 wt% of Mg<sub>2</sub>Ni phase after 100 turns of HPT. It was also possible to identify that phase formation increased along the axial and radial directions of the disc, following the strain increment. This suggests that HPT is a powerful method to synthesize intermetallic compounds that can be difficult to fabricate by conventional means.

Regarding the alloying synthesis process of Mg<sub>2</sub>Ni, the sample with 100 turns showed the highest amount of Mg<sub>2</sub>Ni and the highest storage capacity. Accordingly, it seems this is the optimum number of turns for the hydrogen storage capacity.

Finally, an interesting result of this research is that complete hydrogen absorption by the Mg-Ni system was observed after several weeks of air exposure for all Mg-30 at% Ni samples. This indicates that the HPT-processed samples have good air resistance.

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## Nomenclature

a	a lattice parameter in x,y,y (a,b,c) system	h	thickness of the disc
Abs	absorption	hcp	hexagonal compact structure
Activ	activation	HT	heat treatment
Å	Angström unit	HEBM	high-energy ball milling
at%	atomic percentage	Kα	k alpha radiation
bcc	body-cubic center structure	N	number of HPT turns
c	c lattice parameter in x,y,y (a,b,c) system	r	radius
CP	commercially pure	RT	room temperature
ECAP	equal-channel angular processing	wt%	weight percentage
fcc	face-center cubic structure	γ	equivalent shear strain

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