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## Direct synthesis of $\text{Mg}_2\text{NiH}_4$ from $\text{MgH}_2$ and Ni

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**Abstract.** We showed that the exposure of a pressed mixture of  $\text{MgH}_2$  and Ni powders to a hydrogen atmosphere at 450 °C leads to the direct formation of  $\text{Mg}_2\text{NiH}_4$ . No pre-milling was used. The reaction was carried out at a hydrogen pressure exceeding the equilibrium over  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$ . The pressure invariability during the synthesis evidences the absence of a separate stage of magnesium hydride decomposition and stabilization of the synthesized hydride. The amount of  $\text{Mg}_2\text{NiH}_4$  was determined by the XRD and TDS methods. SEM with EDX microanalysis was used to examine the morphology of the reaction products. The influence of the exposure time and the synthesis temperature on the reaction yield was studied.

**Keywords:** metal hydrides, hydrogen storage materials, solid-state direct synthesis, triple hydride  $\text{Mg}_2\text{NiH}_4$ , intermetallide  $\text{MgNi}_2$

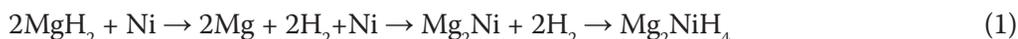
### Introduction

$\text{Mg}_2\text{NiH}_4$  is of interest for solid-state hydrogen storage and electrochemical application. It contains up to 3.6 wt.% of hydrogen. Compared with  $\text{MgH}_2$ ,  $\text{Mg}_2\text{NiH}_4$  has better kinetics of hydrogen absorption and desorption, and a lower temperature (223 °C) corresponding to the equilibrium with the gaseous phase at the pressure of 1 bar. Sustainability in the course of hydrogenation/dehydrogenation cycling is an additional advantage for practical use.

After the article (Reilly, Wiswall 1968) showed that the interaction of intermetallic compound  $\text{Mg}_2\text{Ni}$  with hydrogen results in the reversible formation of  $\text{Mg}_2\text{NiH}_4$ , this route of synthesis was chosen as the primary one.  $\text{Mg}_2\text{Ni}$  can be obtained by laboratory methods (for example, alloying in an induction furnace under argon (Reilly, Wiswall 1968), bulk mechanical alloying and conventional casting techniques (Blomqvist, Noréus 2002; Blomqvist et al. 2002; Mulas et al. 2008)), however, in most cases the commercial-grade material is used.

In addition to hydrogenation of  $\text{Mg}_2\text{Ni}$ , alternative routes for synthesis of  $\text{Mg}_2\text{NiH}_4$  from  $\text{MgH}_2$  and Ni are being actively explored. Most of these studies involve the decomposition of magnesium hydride as an intermediate stage.

The hydriding combustion method reported in (Akiyama et al. 1997;1998; Li et al. 1999; 2001; 2004; 2005; Saita et al. 2003) represents the synthesis of  $\text{Mg}_2\text{NiH}_4$  as a series of successive chemical transformations. A powdered mixture of  $\text{MgH}_2$  and Ni was subjected to heating up to 567 °C that led to the decomposition of  $\text{MgH}_2$  and formation of  $\text{Mg}_2\text{Ni}$  intermetallic compounds from metallic magnesium and nickel. Subsequent cooling in a hydrogen atmosphere results in hydrogen absorption by the intermetallic compound. Thus, the  $\text{Mg}_2\text{NiH}_4$  ternary hydride is the product of the following multistage process:



Another synthesis method based on high-energy ball milling was described in (Martinez-Coronado et al. 2012; Orimo et al. 1997; Polanski et al. 2013). Taking into account the known non equilibrium processes occurring during ball milling and the probability of significant local overheating under these conditions, it is natural to assume a partial decomposition of the hydride and, therefore, the formation of a metal phase. So, the authors' statement about "direct reaction" is questionable.

Herein, we demonstrate another synthesis route of  $\text{Mg}_2\text{NiH}_4$  through direct reaction of magnesium hydride with metallic nickel under moderate pressure-temperature conditions without the intermediate stage of  $\text{MgH}_2$  decomposition. In (Kataoka et al. 2007; Martinez-Coronado et al. 2013; Takamura et al. 2002), similar quasi-hydrostatic syntheses under ultra-high pressures (2–5 GPa) have been reported. We have to note here that there are no available data on the phase behavior of  $\text{MgH}_2$  at the experimental temperatures (700–800 °C) exceeding the magnesium melting point (650 °C). The obvious impossibility of the *in-situ* control of the course of reaction provides no insights into its possible mechanism. Although the thermodynamic estimation shows that the reaction does not require such harsh conditions, this has never been confirmed experimentally.

In contrast to such rigid conditions of synthesis we found that this reaction occurs at a temperature of 450 °C and hydrogen pressures exceeding the equilibrium decomposition pressures of  $\text{Mg}_2\text{NiH}_4$  and  $\text{MgH}_2$ . Such solid-phase interaction that proceeds at a sufficiently low temperature without any intensive mechanical or catalytic assistance is of interest. It should involve mutual penetration of nickel with a melting point of 1453 °C and  $\text{MgH}_2$ , a salt-like substance, via  $\text{Mg}_2\text{NiH}_4$ . The latter, according to (Blomqvist, Noréus 2002; Humphries et al. 2017), is an insulator at 450 °C.

In (Baraban et al. 2022), the growth of hydride film  $\text{Mg}_2\text{NiH}_4$  on the flat surface of nickel foil at 450 °C was considered upon interaction with  $\text{MgH}_2$  powder in hydrogen at pressures exceeding, as in the present study, the decomposition pressures of  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$ . The flat configuration of the substrate-film system allowed the growth mechanism to be established. The kinetics of the increasing amount of the reacted fraction (RF) and XRD results obtained in the present work using powders allow us to state that the mechanism of  $\text{Mg}_2\text{NiH}_4$  hydride synthesis is similar to that described in (Baraban et al. 2022).

## Materials and methods

We used the following methods and equipment. The phase composition and the hydrogen content were determined by 2 ways. i) X-Ray Diffraction (XRD) method using the Bruker "D2 Phaser" (Cu) diffractometer (TOPAS software and Rietveld method). ii) Thermal Desorption Spectrometry (TDS) using custom-built vacuum equipment with RGA100 (Stanford Research Systems). The analytical capabilities of Scanning Electron Microscopy (SEM) using the Carl Zeiss Merlin microscope were expanded with additional X-ray energy dispersive microanalysis system by Oxford Instruments INCAx-act for Energy-Dispersive X-ray spectroscopy (EDX).

Magnesium hydride was synthesized in a high-pressure setup by direct hydrogenation of 99.2% pure magnesium powder with the average particle size of 50–100 micron. The synthesis was performed at pressures of 40–60 bar and temperatures of 420–450 °C. According to XRD and TDS analysis, the hydrogenated samples contain 6.9–7.3 mass% of hydrogen that corresponds to H/Mg ratio of 1.8–1.9. The presence of metallic magnesium and magnesium oxide in the main  $\text{MgH}_2$  phase has been detected by XRD. The second reagent for the  $\text{Mg}_2\text{NiH}_4$  synthesis was nickel powder with the purity of 99.92% and the average particle size of 5 µm.

The preparation of samples for the  $\text{Mg}_2\text{NiH}_4$  synthesis involved thorough mixing of the  $\text{MgH}_2$  and Ni powders at the molar ratio of 2:1 and their subsequent pressing to the density of  $1.9 \pm 0.1 \text{ g/cm}^3$ , which corresponds to 70–75% of the theoretic one for the studied composition. The mass of the samples was

in the range of 0.2–0.5 g. The detailed description of the equipment and the pressing procedure was previously reported in (Elets et al. 2017).

According to the SEM data, after pressing the material is represented by large  $MgH_2$  particles with finer nickel particles embedded between them (Fig. 1).

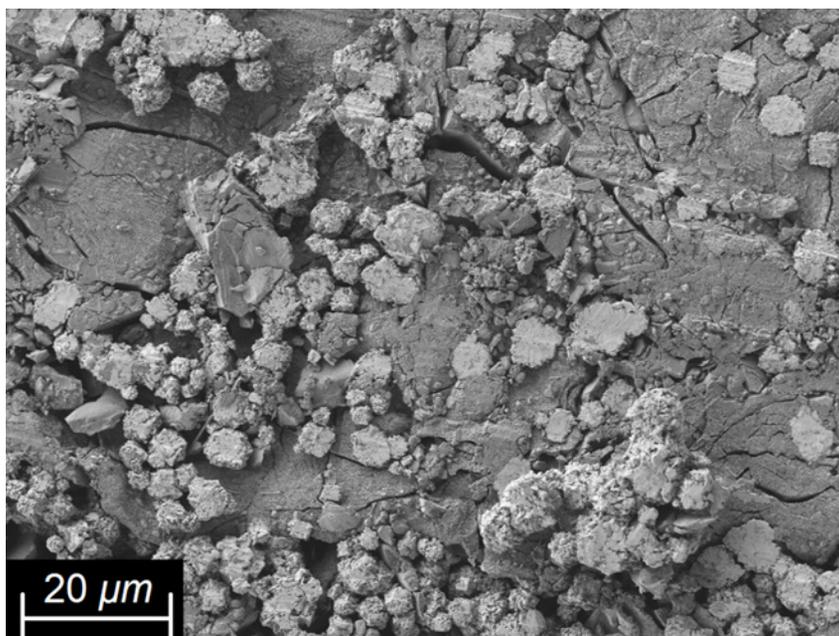


Fig. 1. SEM of the pressed  $MgH_2+Ni$  mixture

The idea of the direct synthesis of  $Mg_2NiH_4$  comes down to a solid-state reaction at a hydrogen pressure high enough to avoid the decomposition of both  $MgH_2$  (the initial reagent) and  $Mg_2NiH_4$  (the reaction product). There are no equilibrium hydrogen pressures for these hydrides for the temperature range over 400 °C reported in the literature. Maximum temperatures are 350 °C for  $MgH_2$  (Leng et al. 2014) and 365 °C for  $Mg_2NiH_4$  (Revesz et al. 2017). In this regard, equilibrium pressures for the temperatures of 400, 425, and 450 °C were determined in preliminary experiments on the decomposition of  $Mg_2NiH_4$  and  $MgH_2$ . They approximately correspond to the middle part of the desorption branches of the P-C diagrams. The results are shown in Table 1. They correlate with the extrapolation of data from the articles (Leng et al. 2014; Revesz et al. 2017) to the indicated temperature range. All the experiments described below were carried out taking these data into account.

Table 1. Hydrogen desorption equilibrium pressures

T, K (T, °C)	673 (400)	698 (425)	723 (450)
$MgH_2$ - Mg	16	25.5	38
$Mg_2NiH_4$ - $Mg_2Ni$	22.6	35.1	48.9

The pressed samples were placed in a stainless steel reactor. After vacuuming, the reactor was filled with hydrogen at a pressure exceeding the equilibrium pressure over  $Mg_2NiH_4$  at the experimental temperature in order to prevent its decomposition. The equilibrium pressures of  $Mg_2NiH_4$  are higher than those of  $MgH_2$ , so the decomposition of the latter did not occur, either. The temperature was kept constant during the synthesis (400–450 °C) for 2–12 hours, then, the reactor was cooled. A slight increase in the hydrogen pressure during heating complied with the gas laws. During the exposure at the constant temperature, the pressure variations did not exceed 0.2 bar.

Fig. 2 shows the characteristic curves of pressure in the reactor and its temperature in the synthesis process (note a gap on the abscissa axis made for clarity). Initially the sample contained 63.9 mg of nickel and 58.5 mg of  $\text{MgH}_2$ . A smooth increase in the hydrogen pressure to 67.5 bar when the sample is heated to 450 °C corresponds to a change in pressure when heating an empty reactor. This indicates the absence of decomposition of  $\text{MgH}_2$  and synthesized  $\text{Mg}_2\text{NiH}_4$ . In the syntheses described in this article we used hydrogen pressures exceeding the pressures of  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$  decomposition.

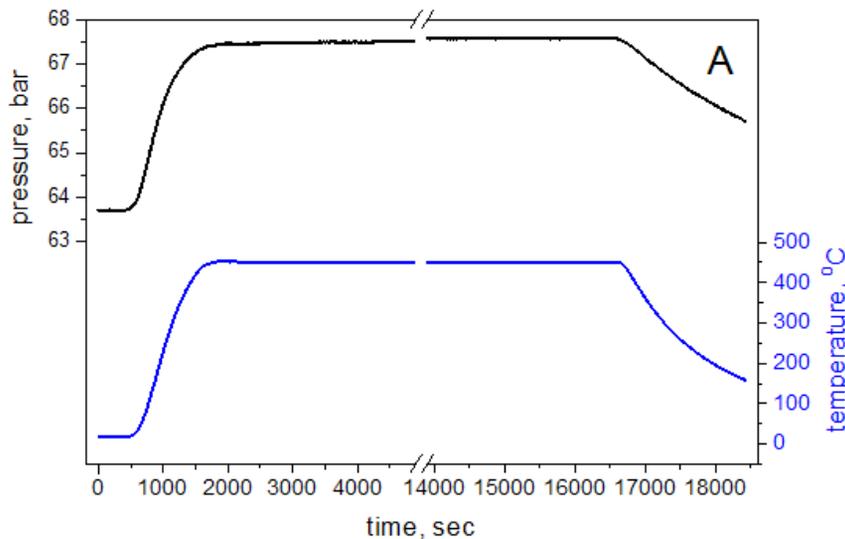


Fig. 2. Pressure and temperature during the synthesis

## Results and discussion

The XRD data on the reaction products obtained under different synthesis conditions are presented in Fig. 3. The exposure at 400 °C for 5 hours does not cause visible changes in the phase composition compared with the initial mixture, while an increase to 425 °C results in the formation of  $\text{Mg}_2\text{NiH}_4$  ternary hydride. The amount of this phase increases significantly with temperature and exposure time, and reaches ~55 mass% after 12 hours at 450 °C. The synthesis parameters and the corresponding phase compositions (in mass%) after 5 hours of exposure are summarized in Table 2. RF stands for the reacted fraction.

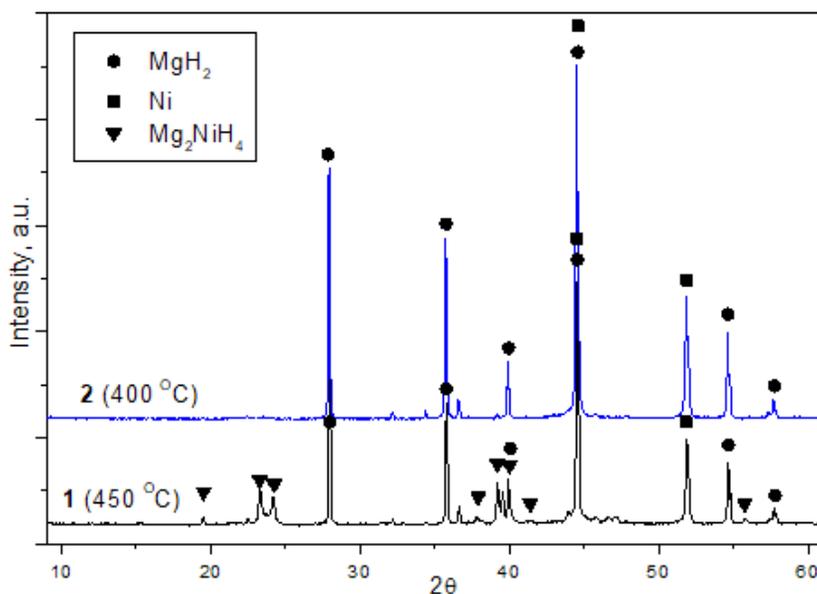


Fig. 3. XRD patterns of the reaction products. Exposure for 5 hours at 450 °C (1) and 400 °C (2)

Table 2. The results of the XRD analysis of reaction products (in percent) and the reacted fraction of  $Mg_2NiH_4$  after a 5-hour exposure at different temperatures and pressures

T, K (T, °C)	673 (400)	698 (425)	723 (450)
P, bar	25.9	39.9	63.4
Phase name (ICDD card number)	mass %		
Mg (03-065-3365)	1.6	1.0	1.3
MgO (01-073-3815)	traces	traces	traces
Ni (03-065-2865)	44.4	36.2	31.8
$MgH_2$ (01-075-7944)	52.2	52.6	40.5
$MgNi_2$ (03-065-4318)	1.0	1.5	1.7
$Mg_2NiH_4$ (01-084-0714)	0.0	8.7	24.7
RF	0.0	0.087	0.247

The  $MgH_2/Mg_2NiH_4$  ratio in the synthesis products was also studied by TDS. The typical sample weight was 3–10 mg. In the case of linear heating at a rate of 0.05 K/s, hydrogen evolution from  $Mg_2NiH_4$  in vacuum began at about 200 °C, while the second peak corresponds to the desorption from  $MgH_2$  (Evard et al. 2010). For illustration, Fig. 4 shows the TDS curves for the samples subjected to 3 (A), 6 (B) and 12 (C) hours of exposure at the reaction temperature. The peaks corresponding to  $Mg_2NiH_4$  and  $MgH_2$  decomposition are clearly separated on the TDS curves. This allows evaluating the hydrogen amount related to each of the processes from the peak areas. With an accuracy of 10%, the resulting values agreed with the XRD data.

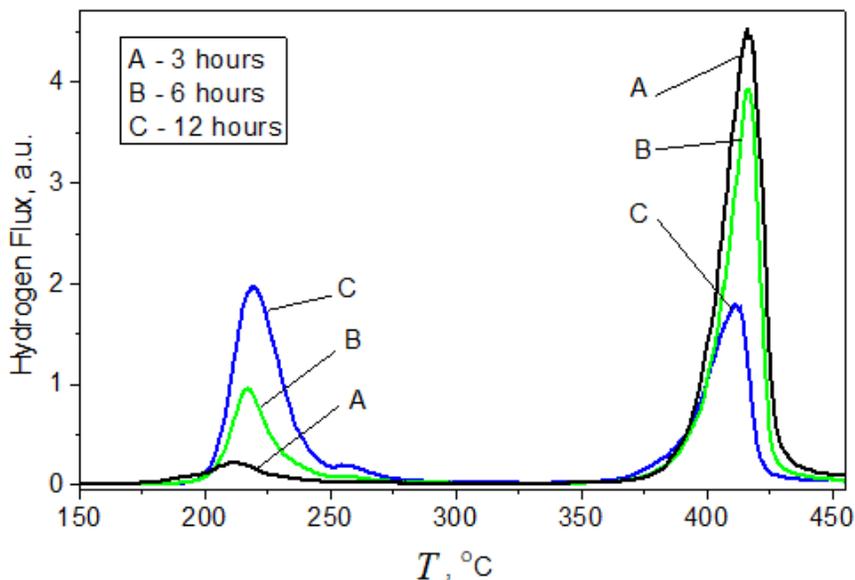


Fig. 4. TDS curves of the samples synthesized for 3 (A), 6 (B) and 12 (C) hours

The SEM image (Fig. 5) demonstrates a significant change in the sample morphology after the synthesis. According to EDX, a large particle in the center contains Mg and Ni at a molar ratio close to 2:1. Smaller particles marked by the arrows at the top right and left contain only Mg (and no Ni). They are likely to refer to the unreacted magnesium hydride.

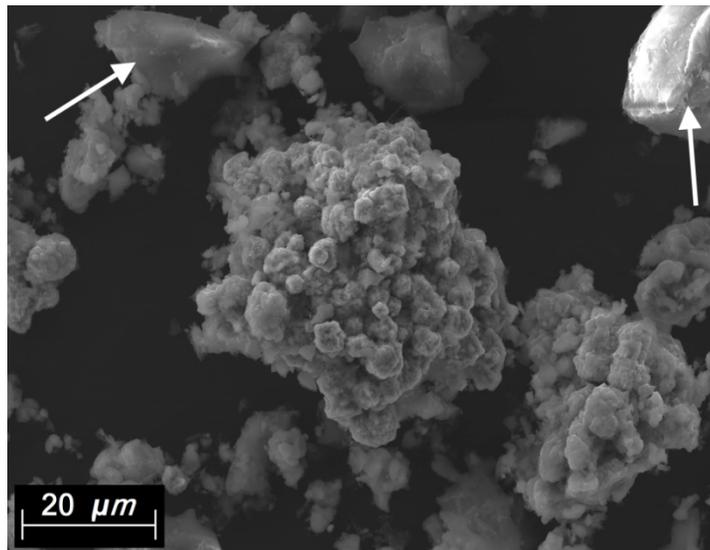


Fig. 5. The SEM image after the synthesis (8 hours, 450 °C)

The influence of the exposure time on the reaction yield was studied in a series of subsequent experiments. They were performed at the temperature of 450 °C under hydrogen pressure exceeding 60 bar. The results calculated from XRD data and expressed in terms of the reacted fraction are shown in Fig. 6. The circles correspond to pressed samples and the squares to unpressed samples. It is worth noting that the same synthesis procedure performed for powder samples, which were not subjected to preliminary pressing, significantly decreased the reaction yield.

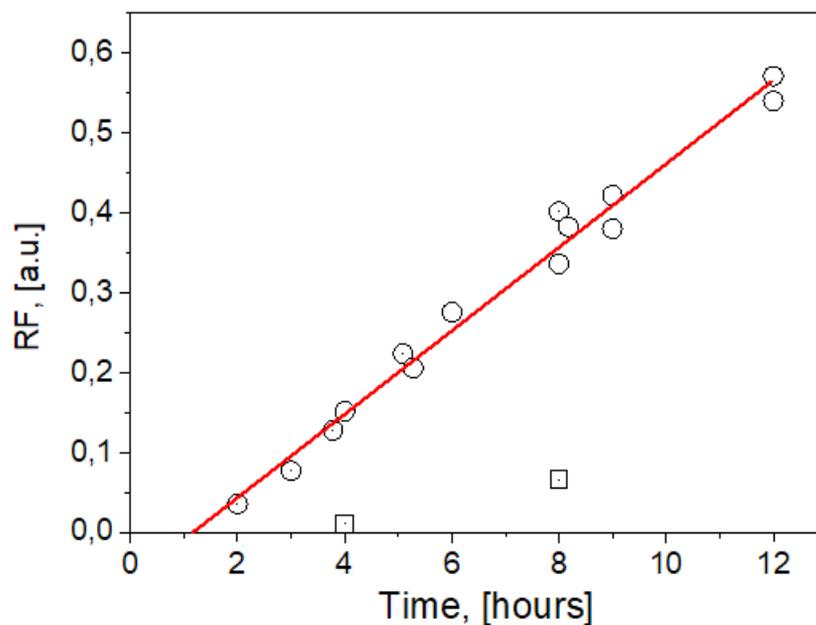


Fig. 6. Reacted fraction of  $Mg_2NiH_4$  synthesis at 450 °C as a function of the exposure time (circles). The squares indicate the unpressed samples

For pressed samples the growth kinetics of the RF is fully consistent with that described in (Baraban et al. 2022) for the same temperature of 450 °C for a planar evolving reaction, namely, linear growth after some delay time (incubation). The red line in the graph represents a linear approximation. The cut-off on the abscissa in our case is 1.16 hours, while it was 1.2 hours in (Baraban et al. 2022), which can be considered a very good match. On the whole, the detailed similarity of the kinetics of the increase

in the amount of synthesized Mg<sub>2</sub>NiH<sub>4</sub> hydride indicates that the mechanisms of synthesis probably coincide as well.

Using the XRD method it was shown in this paper that the delay before the start of Mg<sub>2</sub>NiH<sub>4</sub> synthesis is due to the formation of a Mg<sub>2</sub>Ni sublayer. It grows to a certain thickness, after which the growth of Mg<sub>2</sub>NiH<sub>4</sub> hydride begins. The Mg<sub>2</sub>Ni–Mg<sub>2</sub>NiH<sub>4</sub> interfacial boundary was identified as the place of synthesis. The linearity of Mg<sub>2</sub>NiH<sub>4</sub> layer thickness increase with the synthesis time was explained by a constant rate of nickel atoms diffusion along the MgNi<sub>2</sub> sublayer from the substrate to the Mg<sub>2</sub>Ni–Mg<sub>2</sub>NiH<sub>4</sub> interface.

The analysis of changes in the synthesis rate due to the time factor for powder samples is radically more complex than that for the planar case. The magnesium hydride and nickel powders are mixed and pressed, but their concentrations can vary in different areas of the sample. Another difference is that for the planar samples the magnesium was supplied from the gas phase, while for the powdered samples the magnesium and nickel were pressed together. Therefore, direct diffusion through the solid is more likely. The supply of magnesium through the gas phase cannot be excluded, either. However, the radically lower synthesis rates for the unpressed samples suggest that this channel of magnesium supply is small.

However, the qualitative coincidence of the synthesis kinetics of powder samples with planar samples suggests that the reaction mechanisms are also similar. Firstly, during the incubation process the intermetallic compound MgNi<sub>2</sub> is formed. This process must be associated with the release of some hydrogen. However, the quantity of formed intermetallic compound is small and amounts to 0.5 ± 0.2 mole% for all experimental points, which is negligibly small for our conditions. Note that at the same time the percentage of synthesized Mg<sub>2</sub>NiH<sub>4</sub> varies from 1.3 to 40 mole%. Then, at the Mg<sub>2</sub>Ni–Mg<sub>2</sub>NiH<sub>4</sub> interface the hydride Mg<sub>2</sub>NiH<sub>4</sub> is synthesized, through which Mg and H atoms arrive from MgH<sub>2</sub> via the vacancy mechanism. Following (Baraban et al. 2022), we consider that the constant growth rate of the RF is limited by the constant diffusion rate of nickel atoms through the layer of intermetallic compound MgNi<sub>2</sub>.

The observed chemical transformation can be expressed by equation (2):



Pressure invariability during the synthesis and, therefore, the absence of hydrogen evolution is the main argument in favor of the suggested reaction scheme.

Thus, using the XRD and TDS techniques, we demonstrate that the solid-state direct synthesis of Mg<sub>2</sub>NiH<sub>4</sub> is feasible already at relatively low temperatures starting from 425 °C.

We have to emphasize two main features that are of special interest in the reaction between MgH<sub>2</sub> and Ni.

- Solid-phase interaction proceeds at a sufficiently low temperature without any intensive mechanical or catalytic assistance despite the fact that the reagents are nickel with a melting point of 1453 °C and MgH<sub>2</sub>, which is a salt-like substance at 450 °C.
- No pre-milling or ultra-high pressures were used.

These specific features of synthesis may be of interest. Pressing is technologically simpler than ball milling, while temperature and pressure are significantly lower than in the mentioned articles (Kataoka et al. 2007; Martinez-Coronado et al. 2013; Takamura et al. 2002). Besides, we suggest that the process reported in the present work is applicable for a various set of metals and MgH<sub>2</sub>. This opens a prospect of applying a simple approach to obtaining new intermetallic hydrides when conventional methods of synthesis are not efficient. Novel hydrogen-rich materials could be of particular interest for solid-state hydrogen storage and other applications in hydrogen energy.

## Conclusions

We found that the exposure of a pressed mixture of MgH<sub>2</sub> and Ni in hydrogen at the pressure over 60 bar and the temperature of 450 °C results in the direct synthesis of Mg<sub>2</sub>NiH<sub>4</sub>. The presence of hydrogen prevents decomposition of the magnesium hydride and Mg<sub>2</sub>NiH<sub>4</sub>. Using the XRD, SEM, EDX and

TDS techniques, we investigated this unconventional way of obtaining intermetallic hydride Mg<sub>2</sub>NiH<sub>4</sub> in one step. This solid-state direct synthesis reaction of 2MgH<sub>2</sub> + Ni  $\xrightarrow{\text{H}_2}$  Mg<sub>2</sub>NiH<sub>4</sub> proceeds at low temperatures, starting at 425 °C.

The conditions of the reaction are:

- hydrogen pressure must be higher than the equilibrium pressure with  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$  in order to prevent decomposition of the hydrides. The invariability of the pressure evidences that the reaction proceeds without initial decomposition of magnesium hydride;
- since solid phase mass transfer is responsible for the ternary hydride formation, the pressing of  $\text{MgH}_2$  and Ni powders ensures a good interfacing between the reagents.

The similarities in synthesis kinetics of powder samples and the planar ones described in (Baraban et al. 2022) suggest that the reaction mechanisms are also similar. Firstly, during incubation the intermetallic compound  $\text{MgNi}_2$  is formed. Then, at the  $\text{Mg}_2\text{Ni}$ - $\text{Mg}_2\text{NiH}_4$  interface the hydride  $\text{Mg}_2\text{NiH}_4$  is synthesized, through which Mg and H atoms arrive from  $\text{MgH}_2$  by the vacancy mechanism. The constant growth rate of the RF is limited by the constant diffusion rate of nickel atoms through the layer of intermetallic compound  $\text{MgNi}_2$ .

Further investigation of such reactions is of great importance for a better understanding of the formation of multicomponent hydrides. Besides, it gives a promise of developing an original approach to obtaining new hydrogen-rich materials for various applications in hydrogen storage.

### Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

### Author Contributions

All the authors discussed the final work and took an equal part in writing the article.

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