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Investigation of Hydrogen Storage Characteristics of MgH_2 Based Materials with Addition of Ni and Activated Carbon

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Abstract: Magnesium-based materials are promising as hydrogen storage media due to their high theoretical hydrogen absorption capacity, abundance and low price. The subject of this study are the hydrogen sorption characteristics of the composites 80 wt % MgH_2-15 wt % Ni-5 wt % activated carbon (synthesized from polyolefin wax, a waste product of polyethylene production at low pressure which will be denoted further in the text as POW) and 90 wt % MgH_2-5 wt % Ni-5 wt % POW, prepared by ball milling under argon atmosphere. Structure, phase and surface composition of the samples before and after hydrogenation are determined by XRD and TEM. The maximum absorption capacity value of the composites at a temperature 573 K and after 60 min. of hydrogenation are 5.3 wt % H_2 for the material with higher Ni content and 5.5 wt % H_2 for the other sample. The presence of both additives—nickel and activated carbon derived from POW—has a positive impact on hydrogenation kinetics and the capacity achieved. The results from TEM characterization, e.g., the polycrystalline SAED (selected area electron diffraction) show the presence of graphite, Mg and monoclinic Mg_2NiH_4.

Keywords: Mg-based composites; sorption kinetics; hydrogen storage; carbon materials

1. Introduction

Hydrogen is a renewable and clean energy carrier that can store or deliver a tremendous amount of energy. One of the key problems related with its widespread use is its storage. Finding a solution for the hydrogen storage problem is considered to be the foremost challenge for the hydrogen economy. Some metals and intermetallics form hydrides which can reversibly release H_2 upon heating. Hydrogen storage in metal hydrides is a safe and cost efficient method. One of the promising candidates for hydrogen storage applications is magnesium. Materials based on this lightweight metal have potential as hydrogen storage media due to their high theoretical hydrogen absorption capacity, abundance and low price. To overcome some hindrances of these materials, like slow hydrogen sorption kinetics and high absorption-desorption temperatures, various additives combined with high energy ball milling are used [1–3]. The recently published review by Yartys et al. [3] is focused on the research field of magnesium-based materials for hydrogen energy storage with topics of fundamental and applied studies and a review of the frontiers of both experimental and theoretical research, including nanostructuring, kinetics, thermodynamics and catalysis of magnesium and the hydrides. This review clearly states that Mg-based materials are very attractive for variety of energy applications.

It is established that different carbon compounds, ball milled with Mg or MgH_2, reduced hydrogen sorption temperature, improved kinetics and also prevented MgH_2 particles growth upon milling and hydrogen sorption cycling [4–11]. A considerable improvement of the hydrogen storage properties of Mg, using ball milling of MgH_2 with carbon additives have been reported by Wu et al. [4]. The addition of carbon containing compounds to magnesium leads to milder hydrogen storage temperature and improved hydrogen sorption kinetics of magnesium based materials. Fuster et al. have observed that the catalytic effect of graphite is not related with its morphology, and it is more pronounced when the carbon additive is in higher content and introduced at the beginning of ball milling [4]. The desorption reaction of MgH_2, catalyzed by different carbon materials subjected to microwave irradiation have been investigated by Awad et al. [7]. An enhancement of dehydrogenation rate occurs when the amount of carbon additive, microwave power and milling time are increased.

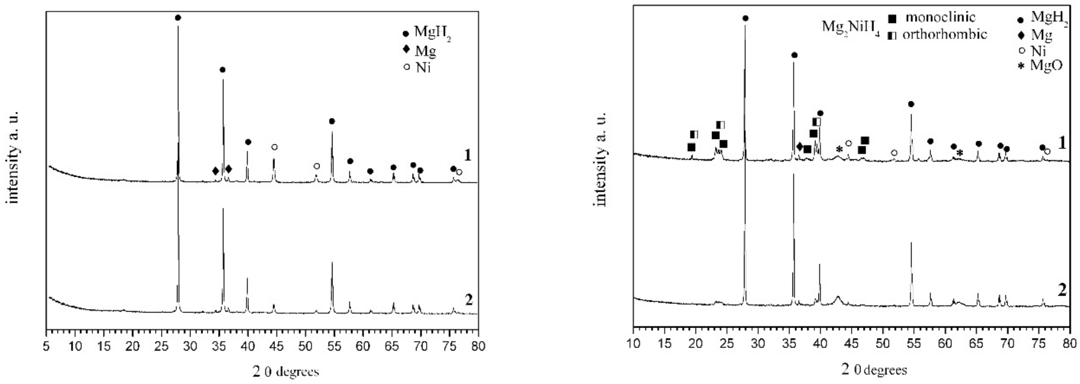
Improvement of hydrogen sorption kinetics can be achieved by adding Ni to Mg and the combination between the positive effect of carbon containing additive and Ni, could result in further benefits of hydrogen sorption properties. The Mg_2Ni forms Mg_2NiH_4 with higher reaction rate, absorbs and desorbs hydrogen at lower temperatures than magnesium, but has theoretical hydrogen storage capacity of 3.6 wt % H_2. Some studies on preparation, crystal structure of Mg_2NiH_4 and the catalytic effect of Ni and some other additives to hydrogen storage characteristics of MgH_2 are published in a series of articles [12–19]. There are two allotropic forms of Mg_2NiH_4—a monoclinic low temperature one and other high temperature with a cubic structure. Synthesis of Mg_2NiH_4 by MgH_2 and Ni is reported by Polanski et al. [14] and Martínez-Coronado et al. [15]. Cermak et al. [12] have shown that catalytic efficiency of Mg_2NiH_4 is considerably higher than that of pure Ni and intermetallic Mg_2Ni. These authors also suggested that Mg_2NiH_4 has un-twinned phase LT1 and micro-twinned phase LT2, two low-temperature modifications, existing below a temperature of 508 K. The phase LT2 is thermodynamically more stable than LT1, and LT1 shows higher catalytic efficiency than LT2 [12]. During the study of the synergistic catalytic effect of $SrTiO_3$ and Ni, on the hydrogen storage properties of MgH_2 at a temperature 593 K and pressure of 2.7 MPa, Yahya et al. [16] have observed formation of Mg_2Ni and Mg_2NiH_4, and these active species contribute to improved hydrogen storage properties of the MgH_2 system. Hydrogen storage materials based on the $Mg(Ni_{1-x}Mn_x)_2$ are synthesized by ball milling and studied as materials for solid state hydrogen storage by Gkanas et al. [18]. The duration of ball milling and the amount of Mn have influence on the hydrogen sorption properties. Prolonged ball milling leads to higher content of $MgNi_2$ and MgO and these species reflect negatively on the hydrogen absorption capacity values and kinetics.

In some of our previous investigations, the effect of graphite and activated carbons derived from low-cost agricultural by-products on the hydrogen sorption properties of magnesium is studied [9,11]. The obtained results drove us to the conclusion that the addition of carbon containing compounds in the materials based on magnesium, has positive impact on their hydrogen sorption properties, leading to an enhanced rate of hydrogenation and higher absorption capacity, compared to pure magnesium. Preparation and characterization of MgH_2-nickel-carbon composites by ball milling under argon atmosphere, and investigation of their hydrogen sorption properties at different temperatures are performed in this study. Two types of additives to MgH_2-carbon containing one synthesized from a waste product, and Ni, with different content, that could lead to formation of Mg_2NiH_4 are used. The aims of these experiments on the one hand are to synthesize at lower temperature, hydrogen pressure and shorter time of ball milling Mg_2NiH_4 and on the other hand to explore the effect of activated carbon prepared from waste product as additive to magnesium based hydrogen storage materials. This work contributes to environmental protection via hydrogen storage and also to resource recovery by using waste product for activated carbon synthesis.

2. Results

2.1. X-ray Powder Diffraction of Ball Milled 80 wt % MgH_2-15 wt % Ni-5 wt % POW and 90 wt % MgH_2-5 wt % Ni-5 wt % POW

The purchased MgH_2 contains some traces of Mg, but the main phase is tetragonal MgH_2. X-ray diffraction patterns of ball milled 80 wt % MgH_2-15 wt % Ni-5 wt % POW and 90 wt % MgH_2-5 wt % Ni-5 wt % POW do not indicate a presence of MgO (Figure 1a). The phases detected in ball milled composites are MgH_2, Ni and some unhydrided Mg. The appearance of new phases is not observed in the samples after ball milling (Figure 1a), which is expected regarding the relatively short milling time.



(**a**) (**b**)

Figure 1. X-ray diffraction patterns of: (**a**) ball milled: (1) 80 wt % MgH_2-15 wt % Ni-5 wt % POW (polyolefin wax) [20] and (2) 90 wt % MgH_2-5 wt % Ni-5 wt % POW; (**b**) after hydrogenation at temperature 573 K and a pressure 1 MPa H_2: (1) 80 wt % MgH_2-15 wt % Ni-5 wt % POW [20] and (2) 90 wt % MgH_2-5 wt % Ni-5 wt % POW.

2.2. Hydrogen Absorption and Desorption Characteristics of 80 wt % MgH_2-15 wt % Ni-5 wt % POW and 90 wt % MgH_2-5 wt % Ni-5 wt % POW

In Figure 2 the hydrogen absorption curves are shown for the 80 wt % MgH_2-15 wt % Ni-5 wt % POW, 90 wt % MgH_2-5 wt % Ni-5 wt % POW and pure MgH_2 and as inset for the first 10 min. of the process of hydrogenation at a temperature of 573 K are also presented. The absorption capacity values obtained at a temperature of 573 K and after 60 min. of hydrogenation are 5.3 wt % H_2 for the material with higher Ni content and 5.5 wt % H_2 for the other sample. For only 1 min. of hydrogenation the 80 wt % MgH_2-15 wt % Ni-5 wt % POW absorbed 1 wt % H_2 at a temperature of 573 K versus 1.1 wt % H_2 for the 90 wt % MgH_2-5 wt % Ni-5 wt % POW. The kinetics hydrogenation curve at a temperature of 573 K for pure magnesium hydride is also presented in this figure. Both samples absorb hydrogen with increased rate and achieved higher absorption capacity than pure MgH_2 without additives. The sample with higher Ni content demonstrated increased rate of hydrogenation in the initial stage of absorption, but slightly lower absorption capacity than the other one with 5 wt % Ni at temperatures of 573 K and 473 K. With a decrease of the absorption temperature at 473 K, the hydrogen absorption rate and absorption capacity value are significantly lower for both samples and the absorption capasity is 1.3 wt % H_2 for the material with 15 wt % Ni and 1 wt % H_2 for the other mixture with 5 wt % Ni.

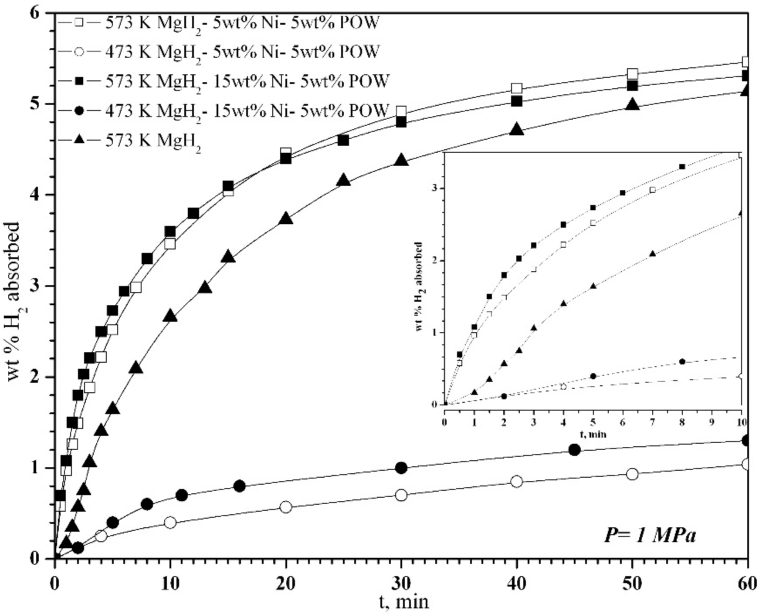


Figure 2. Kinetic curves of hydrogen absorption by the composites 80 wt % MgH_2-15 wt % Ni-5 wt % POW (polyolefin wax), 90 wt % MgH_2-5 wt % Ni-5 wt % POW and MgH_2 at different temperatures.

The hydrogen desorption curves for both samples are presented in Figure 3 and as inset for the first 10 min. of the process the curves at temperatures of 623 and 573 K are also presented. The 80 wt % MgH_2 -15 wt % Ni-5 wt % POW desorbed faster the absorbed H_2 than 90 wt % MgH_2-5 wt % Ni-5 wt % POW up to around 15 min. at temperature of 623 K and a pressure 0.15 MPa H_2 and only for this sample some desorption with low rate is observed at a temperature of 573 K. The hydrogen desorption curve at 573 K for pure magnesium hydride is also presented in Figure 3. The hydrogen desorption process for the both samples with additives of Ni and activated carbon is with much faster rate up to 15 min. than the rate of desorption for the pure MgH_2. After the initial 15 min. of hydrogen desorption the kinetics curves of the 90 wt % MgH_2-5 wt % Ni-5 wt % POW and MgH_2 are identical. The presence of Ni leads to formation of Mg_2NiH_4, which has benefits to the kinetics of absorption and desorption, but decreases the absorption capacity.

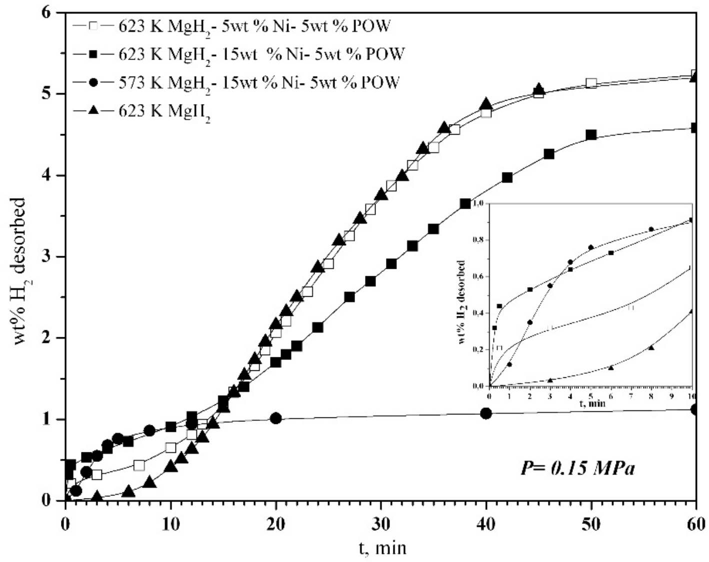
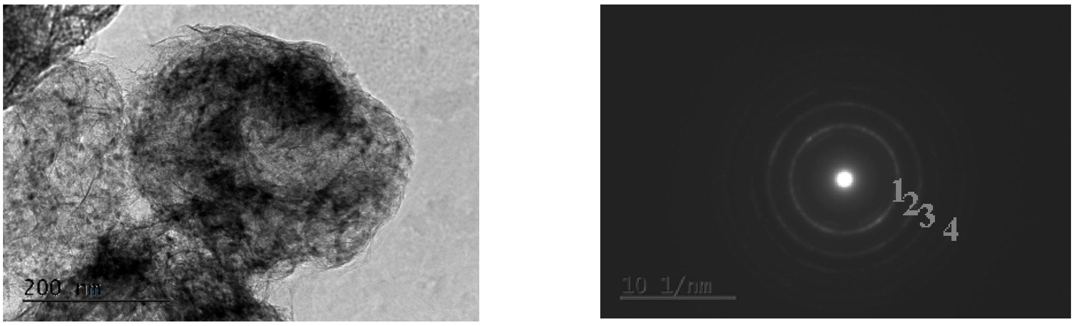


Figure 3. Kinetic curves of hydrogen desorption by the 80 wt % MgH_2-15 wt % Ni-5 wt % POW (polyolefin wax), 90 wt % MgH_2-5 wt % Ni-5 wt % POW and MgH_2.

2.3. Transmission Electron Microscopy Characterization

Transmission electron microscopy characterization is made for the 80 wt % MgH_2-15 wt % Ni-5 wt % POW after hydrogenation. In Figure 4, a bright field micrograph of the composite 80 wt % MgH_2-15 wt % Ni-5 wt % POW after hydrogenation is presented, along with polycrystalline SAED (selected area electron diffraction) patterns. The presence of monoclinic Cc Mg_2NiH_4 phase, graphite, MgH_2 and magnesium are detected. A particle diameter size distribution of 80 wt % MgH_2-15 wt % Ni-5 wt % POW sample, prepared by using Image J program is made (not presented). The average particle diameter derived from this TEM characterization is 8 nm.



(**a**) (**b**)

Figure 4. (**a**) Bright field micrograph and (**b**) polycrystalline electron diffraction with d-spacings as follow: 1: 0.247 nm, 2: 0.214 nm, 3: 0.152 nm, 4: 0.123 nm of the 80 wt % MgH_2-15 wt % Ni-5 wt % POW hydrogenation at a temperature of 573 K and pressure 1 MPa H_2.

2.4. X-ray Powder Diffraction of 80 wt % MgH_2-15 wt % Ni-5 wt % POW and 90 wt % MgH_2-5 wt % Ni-5 wt % POW after Hydrogenation at a Temperature of 573 K and Pressure of 1 MPa H_2

The X-ray diffraction patterns for both samples after hydrogenation at a temperature of 573 K and pressure of 1 MPa H_2 are shown in Figure 1b and confirmed the presence of MgH_2 as main phase, Mg_2NiH_4 in monoclinic and orthorhombic forms and some Mg, Ni and traces of MgO.

3. Discussion

House et al. [17] proved the formation of Mg_2NiH_4 by selected enlarged peaks from the X-ray diffraction patterns of the MgH_2 catalyzed with Ni in the sample ball milled for 10 h. Ball milling for 1h with the parameters used by us for the both prepared samples does not lead to the appearance of Mg_2NiH_4 or other new phases in the diffraction patterns (Figure 1a). The MgO is not detected by X-ray diffraction analysis after ball milling and probably it is presented but below the detection limit.

The composite containing 15 wt % Ni at 573 K after 60 min of hydrogenation reaches absorption capacity of 5.3 wt % H_2 and for the other sample with only 5 wt % Ni the capacity is 5.5 wt % H_2. Practically the obtained absorption capacity values are very close and the difference between them is insignificant. The rate of hydrogenation process at a temperature of 573 K is increased for the 80 wt % MgH_2-15 wt % Ni-5 wt % POW. At the initial stage of hydrogenation up to 2 min. the absorption capacity values are: for the sample with 15 wt % Ni-1.8 wt % H_2 and 1.5 wt % H_2 for the sample with lower amount of Ni. Decreasing the hydrogenation temperature to 473 K reflects negatively on the hydrogen absorption capacity and kinetics for the both samples. However, the mixture 80 wt % MgH_2-15 wt % Ni-5 wt % POW has demonstrated higher absorption capacity and increased absorption rate at a temperature of 473 K than 90 wt % MgH_2-5 wt % Ni-5 wt % POW. Both samples have demonstrated improved kinetics of hydrogen absorption than MgH_2 without any additives. The final absorption capacity values at 573 K do not differ significantly, e.g., for the 90 wt % MgH_2-5 wt % Ni-5 wt % POW is 5.5 wt % H_2, for the 80 wt % MgH_2-15 wt % Ni-5 wt % POW is 5.3 wt % H_2 and for MgH_2 is 5.1 wt % H_2 after 60 min of hydrogenation. Regarding hydrogen absorption curves, the ternary hydride Mg_2NiH_4 is formed after only few cycles of hydrogenation/dehydrogenation at T = 573 K and

P = 1 MPa for absorption and T = 623 K and P = 0.15 MPa for desorption. Comparing these results with some obtained before lead to the conclusions that adding nickel has great effect on the kinetics. For the first 2 min of hydrogenation process at same experimental conditions 95 wt % MgH_2-5 wt % POW absorbed 1.1 wt % H_2 [11] which is around only 60% of the capacity obtained by the 80 wt % MgH_2-15 wt % Ni-5 wt % POW for the same time and experimental conditions.

About half of the absorbed hydrogen is released after 28 min of dehydrogenation by the 80 wt % MgH_2-15 wt % Ni-5 wt % POW at temperature 623 K and a pressure 0.15 MPa H_2. Most probably due to the higher content of Mg_2NiH_4 in the mixture of MgH_2 and 15 wt % Ni shows faster desorption, but only up to 15 min from the process. Some very slow desorption at 573 K is detected only for the 80 wt % MgH_2-15 wt % Ni-5 wt % POW and this should be associated also with higher Ni content and as a result increased Mg_2NiH_4 presence. The MgH_2 shows very slow hydrogen desorption kinetics at 623 K up to first 15 min of the process, but after that its desorption curve overlap this of the 90 wt % MgH_2-5 wt % Ni-5 wt % POW. At same experimental conditions 95 wt % MgH_2-5 wt % POW desorbed hydrogen with slower kinetics for the first 5 min of the process than these composites with addition of nickel [11]. These positive effects on the kinetics can be attributed to the Mg_2NiH_4 formation. Definitely, when this ternary hydride is in higher amount in the samples based on MgH_2 thus reflects positively on the sorption kinetics and lead to lower hydrogenation and dehydrogenation temperatures.

The 80 wt % MgH_2-15 wt % Ni-5 wt % POW consists of fine particles and they enhance the hydrogen diffusion and hydride phase formation, thus could be beneficial of the hydrogen sorption properties. The TEM characterizations of 80 wt % MgH_2-15 wt % Ni-5 wt % POW are confirmed the formation of ternary hydride Mg_2NiH_4 with low temperature monoclinic structure.

Some published results by other authors also confirmed the formation of Mg_2NiH_4 starting by MgH_2 and Ni and in some studies other additives were used. The Mg-Ni-Fe alloy obtained by reactive ball milling showed fast hydrogenation rate at the beginning of the process and absorbed 3.3 wt % H_2 at temperature 593 K and a pressure of 1.2 MPa H_2 [19]. The X-ray diffraction patterns of Mg-Ni-Fe after hydrogenation/dehydrogenation cycling confirmed a presence of Mg_2Ni. A study of the catalytic effect of $SrTiO_3$ and Ni on the hydrogen storage properties of the MgH_2 have been carried out by Yahya et al. [16]. At temperature of 593 K and a pressure 2.7 MPa H_2 the Mg_2NiH_4 were formed and help to improve the hydrogen storage properties of MgH_2 system. House et al. [17] prepared MgH_2 materials catalyzed with Ni by ball milling with different duration. As milling time increased up to 10 h, more Ni was transformed into Mg_2NiH_4 and this cause degradation of hydrogen absorption capacity value. The theoretical absorption capacity value of Mg_2Ni is around twofold lower than that of magnesium and this negative effect is expected. Recently, Gkanas et al. [18] reported their investigation on a new hydrogen storage materials of the type $Mg_2(Ni_{1-x}Mn_x)_2$. The stored hydrogen by these intermetallic phases ball milled for 10 or 20 h were around 1 wt % H_2 at a temperature of 573 K and a twofold higher hydrogen pressure than this used in our study, e.g., 2 MPa. The hydrogen desorption was observed at temperatures 573 K and 523 K and at a pressure 0.05 MPa H_2. These materials demonstrated fast absorption and desorption kinetics, and also desorption at lower temperatures, but with very low sorption capacity. The parameters of ball milling and the conditions of hydrogenation/dehydrogenation used by us are different, but by an easier and faster way we obtained materials that demonstrate relatively fast sorption rate and higher capacity. As is illustrated by the obtained results and characterizations both monoclinic and orthorhombic Mg_2NiH_4 type phases are formed in the samples and have positive effect on the absorption and desorption kinetics.

The combination of these two types of additives-nickel and activated carbon POW results to improved hydrogen sorption properties for the 80 wt % MgH_2-15 wt % Ni-5 wt % POW and 90 wt % MgH_2-5 wt % Ni-5 wt % POW. These investigations confirmed the appearance of Mg_2NiH_4 at these shorter ball milling treatment, lower temperatures and pressure reported in the literature. Moreover, in the both samples $MgNi_2$ is not detected after 10th cycle of hydrogenation at a temperature of 573 K and pressure 1 MPa H_2. The $MgNi_2$ phase does not form hydride and consume a part of magnesium, e.g., reflecting negatively on the capacity and the kinetics. Starting from MgH_2 and Ni mixtures eliminated the formation of the $MgNi_2$ phase. The complete reaction of nickel and MgH_2 to Mg_2NiH_4 is not observed and some Ni is detected in the both samples after hydrogenation. It seems that this method of Mg_2NiH_4 synthesis is easier, faster and gives the opportunity to avoid the $MgNi_2$ appearance.

In these materials based on MgH_2 further improvement of hydrogen sorption kinetics probably could be observed at different ball milling parameters or/and for the samples with other composition, e.g., with increased amount of nickel. The last option should be carefully précised because of diminution of the absorption capacity when the nickel content is increased.

4. Materials and Methods

The activated carbon is prepared from a polyolefin wax, a waste product of polyethylene production at low pressure, submitted to pyrolysis and steam activation, and used as additive in the preparation of MgH_2 based materials. More detailed procedure for activated carbon synthesis can be found elsewhere [9]. The MgH_2 with purity 98% and Ni powder (99.7%) are purchased from Sigma Aldrich (St. Louis, MO, United States).

4.1. Ball Milling in a Planetary Mill

Mixtures of MgH_2, Ni and carbon additive, in the corresponding ratio of 80 wt % MgH_2-15 wt % Ni-5 wt % POW and 90 wt % MgH_2-5 wt % Ni-5 wt % POW, are ball milled under Ar atmosphere in a planetary mono mill Pulverisette 6 Fritsch (Fritsch, Idar- Oberstein, Germany). The parameters of ball milling are: the rotation speed of 200 rpm for duration of 1 h, ball to sample weight ratio 10:1 in a stainless steel vial (volume ca. 80 cm^3) and balls with diameter 10 mm.

4.2. Hydrogen Sorption Measurements

Absorption and desorption kinetics of the composites, denoted, are studied with volumetric Sievert's type apparatus at different temperatures. The absorption measurements are carried out at temperature 473 and 573 K, and a pressure of 1 MPa H_2, while desorption is investigated at $T = 623$ and 573 K, and $P = 0.15$ MPa. The both samples are subjected to at least 10 cycles of hydrogenation/dehydrogenation and the best cycle at each temperature is presented in Figures 2 and 3. The hydrogen sorption kinetics curves for the 80 wt % MgH_2-15 wt % Ni-5 wt % POW are published before in [20].

4.3. X-ray Diffraction and TEM Analysis

The composition of the starting compounds and of the samples, after ball milling and hydrogenation, are determined by XRD with Cu Kα radiation (Powder X-ray Diffractometer Bruker D8 Advance with a LynxEye detector, Bruker, Karlsruhe, Germany). The sample with higher amount of Ni after hydriding is examined also by TEM (TEM HR STEM JEOL JEM 2100 with GATAN Orius 832 SC1000 CCD Camera, JEOL, Tokyo, Japan) at accelerating voltage of 200 kV. The preparation procedure of the specimen is consisted of dispersing them in ethanol by ultrasonic treatment for 6 min. The suspensions are dripped on standard holey carbon/Cu grids. The sample is exposed briefly to air during transfer to the TEM holder. Some part of TEM characterizations were published before in [20].

5. Conclusions

The maximum achieved absorption capacity values at a temperature of 573 K and after 60 min. of hydrogenation are 5.3 wt % H_2 for the material with higher Ni content and 5.5 wt % H_2 for the other sample. The presence of both additives—Ni and activated carbon derived from a polyolefin wax, a waste product of polyethylene production at low pressure—has a positive impact on hydrogenation kinetics and leads to relatively high absorption capacity. The results from XRD and TEM characterizations after hydrogenation, e.g., the polycrystalline SAED (selected area electron diffraction) show the formation of monoclinic and orthorhombic Mg_2NiH_4 in the both samples after hydrogenation. Regarding, the possible practical application of these materials, the hydrogen absorption and desorption temperatures should be lower than those, used in this study.

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Conflicts of Interest: The authors declare no conflict of interest.

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