Materials Science-Poland, 32(3), 2014, pp. 385-390
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-014-0218-9

Hydrogen desorption kinetics of MgH_2 synthesized from modified waste magnesium

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In the present study, hydrogen desorption properties of magnesium hydride (MgH_2) synthesized from modified waste magnesium chips (WMC) were investigated. MgH_2 was synthesized by hydrogenation of modified waste magnesium at 320 °C for 90 min under a pressure of 6×10^6 Pa. The modified waste magnesium was prepared by mixing waste magnesium with tetrahydrofuran (THF) and NaCl additions, applying mechanical milling. Next, it was investigated by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) techniques in order to characterize its structural properties. Hydrogen desorption properties were determined by differential scanning calorimetry (DSC) under nitrogen atmosphere at different heating rates (5, 10, and 15 °C/min). Doyle and Kissenger non-isothermal kinetic models were applied to calculate energy (E_a) values, which were found equal to 254.68 kJ/mol and 255.88 kJ/mol, respectively.

Keywords: *hydrogen desorption; magnesium hydride; kinetics; waste magnesium chips*

1. Introduction

In recent years there has been considerable interest in magnesium hydride (MgH_2) systems for generating pure hydrogen for portable fuel cells because of its acceptable hydrogen storage capacity (7.6 wt.%), low cost and light weight [1, 2]. Nevertheless, the high desorption temperature and poor sorption kinetics makes them useless in practical applications. Therefore several methods have been applied to overcome these issues. Especially, reduction of particle-grain size and addition of a catalyst resulted in the improvement of the surface properties and sorption kinetics of MgH_2 [3–10]. Chemical modification and composite with graphite were also applied [11–17].

DSC technique is widely used for measurement of hydrogen desorption temperature of MgH_2. Recently, Jin et al. [18] reported on the effect of halide additives on decomposition temperature of MgH_2. They performed the DSC measurement to determine the decomposition temperature of MgH_2. It was noted that the decomposition temperature range of NbF_5 is wider than that of other transition metal fluorides. Yano et al. [19] investigated the thermal and kinetic properties of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and a mixture of RDX/MgH_2 by DSC. They also calculated the activation energy (E_a) and pre-exponential factor (k_0) based on the data of DSC experiments, using the Kissinger and Ozawa methods. They concluded that E_a of the mixture RDX/MgH_2 is lower than that of RDX.

Bohmhammel et al. [20] conducted the kinetic investigations using the isothermal DSC study for the Mg/MgH_2 system. They showed the dependence of reaction rate on hydrogen pressure (p_0), temperature and described the sample morphology based on the experimentally obtained DSC-signals. Varin et al. [21] reported the hydrogen desorption properties of MgH_2 mechano-synthesized for 75 h with 2 wt.% various forms of nickel powder made by the nickel carbonyl decomposition process. They found by DSC investigations that desorption temperatures (onset and maximum rate) were reduced of 30 – 50 °C with respect to the DSC desorption temperatures of the synthesized undoped MgH_2 powder.

Although many investigations of MgH_2,

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modified MgH_2 and MgH_2 composites have been performed, no studies of the hydrogen desorption kinetics of MgH_2 synthesized from modified waste magnesium have been conducted. Therefore, in this study, such investigations were undertaken using modified waste magnesium prepared by mechanical milling of waste magnesium chips with tetrahydrofuran (THF) and NaCl additions before the MgH_2 production. The produced MgH_2 was next characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller analyses (BET) and differential scanning calorimetry (DSC). Additionally, Doyle and Kissinger non-isothermal kinetic models were applied to calculate the kinetic parameters (E_a and k_0).

2. Experimental details

2.1. Materials

2.1.1. Preparation and characterization of modified waste Mg chips

In the present study, waste magnesium chips (WMC) were used as a raw material for magnesium hydride (MgH_2) synthesis. WMC were the end product of plastics machining process from the gold manufacturing factory. In Table 1 there are shown results of chemical analysis (major and minor elemental analyses), specific surface area, melting temperature of waste magnesium chips, obtained by XRF, BET and DSC, which were presented in our previous work [22].

Modified waste magnesium was prepared by mechanical milling of magnesium waste with tetrahydrofuran (THF) and inorganic salt (NaCl) before the hydrogenation procedure. Before the mechanical milling, the components were first cleaned in an ultrasonic cleaner in THF for 0.5 h and next milled in a planetary type ball-milling apparatus (Fritsch, Pulverisette 6) at 300 rpm. The milling process was performed with the ball-to-powder weight ratio fixed at 70:1 in the presence of THF organic solvent (ml/g: 9/1) and 5 wt.% of NaCl. Wet milling of the modified waste magnesium was carried out for 15 h and all materials were stored in a glove box to minimize the oxidation. The crystal structure, microstructure, particle and crystallite size of the modified waste magnesium were analyzed and the results are shown in Table 2. The samples were characterized by X-ray diffraction (XRD, Philips Panalytical X'Pert-Pro, CuKα radiation), Brunauer-Emmett-Teller analyses (BET, Micromeritics ASAP 2020) N_2 adsorptive gas with multipoint modes, X-ray fluoresce spectrometry (XRF, Minipal 4) and scanning electron microscopy (SEM, JEOL JSM 5410 LV).

2.2. Synthesis of MgH_2

Modified WMC powders were loaded into a reactor and the sample was degassed at 320 °C under vacuum to remove the humidity/oxide from the magnesium surface. MgH_2 was prepared by hydrogenation of modified WMC powders at 320 °C for 90 min under a pressure of 6×10^6 Pa and the powder mixture was cooled down to room temperature under hydrogen atmosphere. Stainless-steel reactor was pressurized with hydrogen in the range of about atmospheric pressure to 2×10^7 Pa and heated up to 550 °C. The temperature and pressure was controlled automatically via a microprocessor-based PID controller. Samples after the hydrogenation were characterized by XRD analysis to check the phase composition.

2.3. Hydrogen desorption kinetics of MgH_2

Hydrogen desorption kinetics of produced MgH_2 was investigated using a DSC apparatus (Perkin Elmer Diamond). Hydrogen desorbed from the sample in non-isothermal conditions (heating rate of 5, 10, 15 °C/min in temperature up to 500 °C) according to the following chemical reaction:

$$MgH_{2(s)} \rightarrow Mg_{(s)} + H_{2(g)} \tag{1}$$

Kinetic parameters (E_a and k_0) were obtained using non-isothermal methods by Kissinger and Doyle. The Kissinger method is based on the fitting of experimental data applying the following equation:

$$\ln\frac{\beta}{T_m^2} = \frac{-E_a}{R}\left(\frac{1}{T_m}\right) + \ln\frac{nk_0R(1-\alpha_m)^{n-1}}{E_a} \tag{2}$$

Table 1. Structural properties of waste magnesium chip

Major elements (XRF analysis)	93.30 % Mg and 3.67 % Al
Minor elements (XRF analysis)	Zn (0.88 %), Mn (0.90 %), S (0.08 %), Ca (0.11 %), Cr (0.03 %), Fe (0.93 %), Cu (0.14 %)
Specific surface area (BET analysis)	0.08 m^2g^{-1}
Melting temperature (DSC analysis)	405 °C

Table 2. Structural properties of modified waste magnesium.

Composition (XRF analysis)	88.86 % Mg, 3.49 % Al, 5.00 % NaCl
Minor elements (XRF analysis)	Zn (0.83 %), Mn (0.85 %), S (0.07 %), Ca (0.10 %), Cr (0.03 %), Fe (0.88 %), Cu (0.13 %)
Specific surface area (BET analysis)	239.79 m^2g^{-1}
Particular size (SEM analysis)	16.05 µm
Melting temperature (DSC analysis)	>500 °C

where: T_m is maximum temperature point at derivative mass loss curve for different heating rates, R is gas constant (8.314 $Jmol^{-1}K^{-1}$), β is heating rate ($K{\cdot}s^{-1}$), α_m is decomposition fraction at T_m (%), k_0 is pre-exponential factor (s-1) and n is reaction order. E_a and k_0 can be determined from the slope and the intercept of the curve [2], respectively [23].

In the Doyle model (equation 3), values of log β are plotted against $1/T_m$ giving parallel lines with $0.4567E_a/R$ slope and c1 is a constant. The E_a and k_0 can be calculated from the slopes of the lines evaluated by equation 3 and equation 4 [24].

$$-\log\beta = 0.4567\left(\frac{E_a}{RT_m}\right) + c1 \tag{3}$$

$$k_0 = \exp\left(\frac{E_a}{RT_m}\right)\frac{\beta E_a}{RT_m} \tag{4}$$

3. Results and discussion

3.1. Structural properties of modified waste Mg

In Fig. 1 the XRD pattern of modified waste Mg powders is shown. According to the XRD analysis result, Mg (PDF: 00-035-0821) is the main phase, while the NaCl (PDF: 01-075-0306) and Al–Ag–Mg ($Al_{60}Mg_{38}Ag_2$) complexes are present in the sample in a low amount. Characteristic peaks of Mg are observed at diffraction angles of 36.63° (100 % intensity) and 34.34° (82.06 % intensity) in 2θ the pattern. Another important information from this studies is that the metallic structure had not changed after ball milling and that NaCl did not react with Mg.

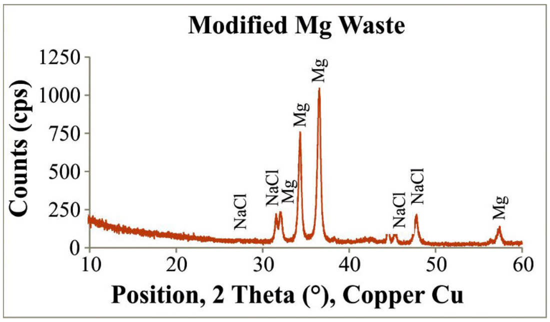

Fig. 1. XRD pattern of modified waste magnesium.

In Fig. 2 the SEM images of modified waste Mg powders are shown at different magnifications as: 39 ×, 150 ×, 1000 ×, 2000 ×. Wet milling in the presence of organic solvent THF was more effective than dry milling. During the ball milling the flow of the liquid also abraded the particles and acted as a shield to prevent the grinding of smaller particles. Thus, homogeneous and regular particles were obtained. Furthermore, the NaCl addition improved the surface properties causing cracking of the oxide layer and formation of micro cracks on the surface. The average particle size was calculated on the basis of SEM results and it was equal to 16.05 ± 1.75 µm. Table 2 lists the structural properties of the modified waste Mg powders. As it can be seen, after the modification the BET surface area has increased from 0.08 m^2g^{-1} to 239.79 m^2g^{-1} due to formation of micro cracks on the surface.

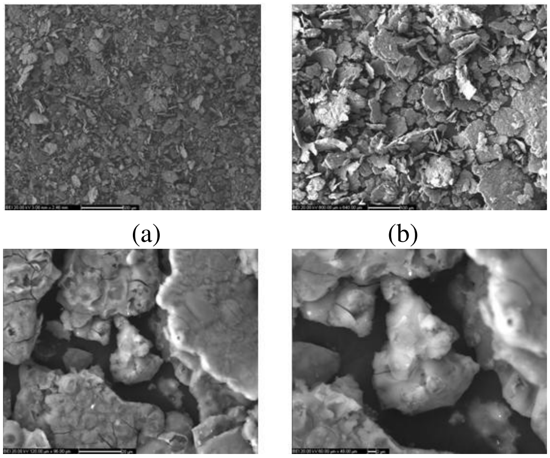
(a) (b)
(c) (d)

Fig. 2. SEM images of modified waste magnesium at (a) 39 ×, (b) 150 ×, (c) 1000 ×, (d) 2000 × magnifications.

3.2. Synthesis of MgH_2

The XRD of hydrogenated modified waste Mg powders obtained at 320 °C for 90 min under a pressure of 6×10^6 Pa are shown in Fig. 3. As it is seen, the main phase in the sample was β-MgH_2 (PDF: 01-074-0934) with the small amount of NaCl. There are some peaks that are related to the small amount of Mg. The peaks appearing at 34.34°, 35.54° and 57.55° diffraction angels are characteristic of the metallic Mg of the hexagonal crystal structure.

3.3. Hydrogen desorption kinetics of MgH_2

DSC curves of the MgH_2 at different heating rates are shown in Fig. 4. The sharp endothermic peaks observed at 447.61, 459.92 and 464.62 °C at 5, 10, 15 °C/min can be assigned to the decomposition of β-MgH_2. This observation agrees with previous studies, which reported the endothermic peak with an onset temperature around 441 °C [25, 26]. Heating rate has a significant effect on the hydrogen desorption of MgH_2. The increase in the heating rate leads to a less uniform heat distribution and higher temperature gradient. It can be seen that all temperatures have been shifted to higher values with increasing heating rate.

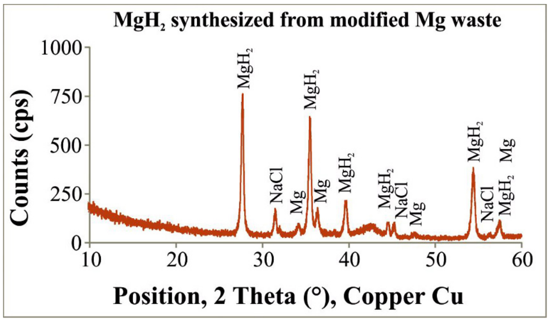

Fig. 3. XRD pattern of MgH_2 synthesized from modified Mg waste.

Applying the Kissinger method, T_m at different heating rates was determined from DSC curves with the assumption that weight loss at T_m is constant. E_a value was calculated from the slope of the kinetic curve given in Fig. 5 and its value is equal to 255.88 kJ/mol (Table 3).

Table 3. Hydrogen desorption kinetic parameters of MgH_2.

Parameters	Doyle	Kissinger
E_a(kJ/mol)	254.68	255.88
k_0(min^{-1})	2.16×10^5	1.06×10^{17}

In the Doyle method, the values of log β plotted against $1/T_m$ are straight lines for the rate of heating equal to 5, 10 and 15 °C/min, which is shown in Fig. 5, and the calculated E_a value equals to 254.68 kJ/mol at first reaction order (Table 3).

The equations describing the hydrogen desorption reaction rate of MgH_2 can be expressed as follows:

$$\frac{d\alpha}{dt} = 2.16 \times 10^5 e^{-(254680/RT)} (1-\alpha)^1 \quad \text{for Doyle model} \tag{5}$$

$$\frac{d\alpha}{dt} = 1.06 \times 10^{17} e^{-(255880/RT)} (1-\alpha)^1 \quad \text{for Kissinger model} \tag{6}$$

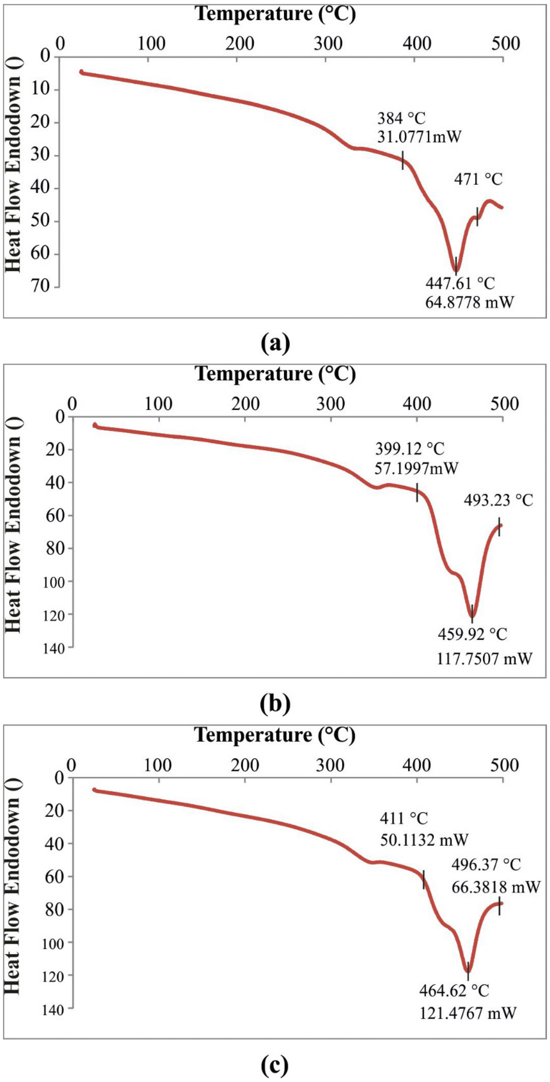

Fig. 4. DSC curves of MgH_2 synthesized from modified Mg waste at different heating rates (a) 5 °C/min, (b) 10 °C/min, (c) 15 °C/min.

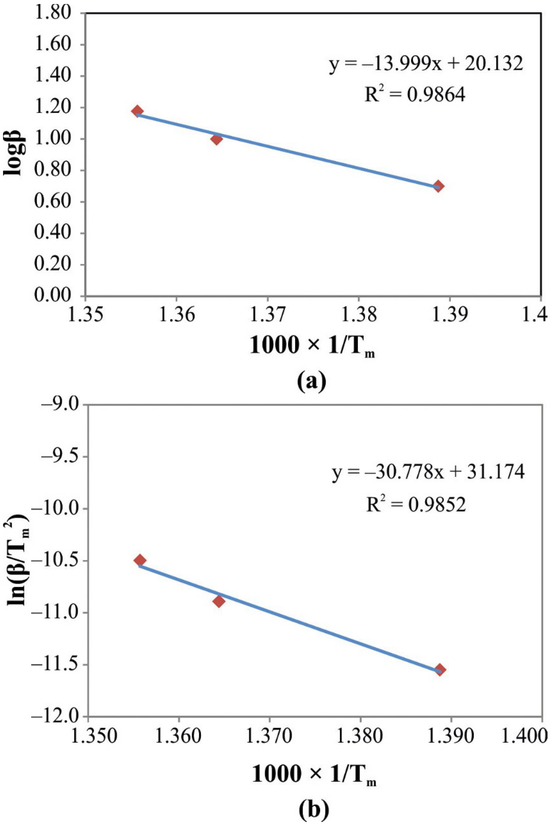

Fig. 5. Kinetic plots of hydrogen desorption of MgH_2, (a) Doyle model, (b) Kissinger model.

4. Conclusions

Waste magnesium chips can be used for the hydrogen storage after modification by mechanical milling with tetrahydrofuran (THF) and NaCl followed by the hydrogenation at 320 °C under a pressure of 6×10^6 Pa of H_2. The observed desorption temperatures of the produced β-MgH_2 were equal to 447.61, 459.92 and 464.62 °C for the heating rates of 5, 10, 15 °C/min, respectively. It was found that the increase in the heating rate leads to the increase of decomposition temperature. The activation energy values of β-MgH_2 desorption calculated by the Kissinger and Doyle models were almost the same and they were equal to 255.88 and 254.68 kJ/mol, respectively.

Because of the high hydrogenation and decomposition temperature of β-MgH_2 the future study should be performed to lower either temperature or hydrogen desorption.

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Received 2014-03-18
Accepted 2014-06-11