Desorption behaviour of MgH₂-Ni-SiC prepared by ball milling for hydrogen storage material application

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Abstract. Magnesium (Mg) is one potential candidate that can be used as a hydrogen absorbent. Theoretically, Mg can absorb large amounts of hydrogen up to 7.6 wt.%. However, the kinetic reaction of Mg in absorbing hydrogen takes at least 60 minutes when it occurs at high temperatures (300–400 °C). The purpose of this study is to increase hydrogen desorption capacity and the working temperature of the MgH₂-Ni-SiC-based storage system. The materials preparation was done with mechanical alloying technique. The milling process was varied for three different times of 5 h, 10 h and 15 h, with the two catalyst ratios of five wt.% and ten wt.% and the speed of 350 rpm. X-Ray Diffraction (XRD) measurement results revealed that the sample has successfully become nano-sized crystals with the dominant phase of MgH₂ and the minor phases of Ni and SiC. The irregular shape of the particles and their non-homogeneous size are known from the Scanning Electron Microscopy (SEM) results, which are caused by agglomeration. The best hydrogen desorption capacity of up to 2.6 % and the lowest temperature desorption of was 365 °C was obtained for samples that were milled for 10 hours with five wt.% Ni-SiC catalyst.

Keywords: Magnesium, hydrogen storage, reactive mechanical alloying, catalyst, silicon carbide.

1. Introduction
Magnesium (Mg) and Nickel (Ni) are hydrogen absorbent materials that are potential for applications in fuel cell vehicles. Theoretically, Mg is capable of absorbing large amounts of hydrogen (7.6 wt.%), which exceeds the target of the International Energy Agency (IEA) for 5 wt.% absorption capacity and temperature of absorption-desorption of ≤100 °C [1]. Moreover, Mg is a lightweight and easily obtained element at affordable prices, making it considered to be studied today. But the drawback is that Mg has a prolonged kinetic reaction and high operating temperature in absorbing hydrogen, it takes at least 60 minutes and a temperature of 300 °C. The provisions of the IEA state that the material to be used as a hydrogen absorbent must be able to show the performance of hydrogen absorption occurring at temperatures below 100 °C in a short time [2–5].

Several researchers have studied magnesium alloys with various manufacturing methods and variations in the alloying elements. Ranjbar et al. [6] have carried out research using MgH₂ as a matrix with SiC particles dispersed in the matrix. After a small amount of SiC (5 wt.%) has been inserted in the matrix, the materials are capable of absorbing hydrogen as much as 6.3 wt.% at a temperature of 350 °C in a very short time (5 minutes).
2nd International Conference on Current Progress in Functional Materials 2017  IOP Publishing
IOP Conf. Series: Materials Science and Engineering 496 (2019) 012062  doi:10.1088/1757-899X/496/1/012062

Figure 1. XRD profile on MgH₂ + Ni + SiC material with a catalyst of 5 wt% SiC and three milling time variations of 5 hours, 10 hours and 15 hours

Other studies were done using reactive ball milling technique for double catalyzed Ni and SiO₂ inserted in MgH₂ material with four variations of SiO₂ wt.% of 3, 5, 10 and 15. The result of Differential Scanning Calorimetry (DSC) showed that the lowest temperature for hydrogen desorption to occur is reached at 361 °C for 15 wt. % of SiO₂ catalyst [7–8]. The temperature of the hydrogen desorption temperature of is too high for its application in the vehicle industry. Several researchers have carried out further material and involving nano-sized catalysts [9,10] and double nano-sized catalyst [11] to improve hydrogen absorption/desorption characteristics of MgH₂ material to be applied as a hydrogen storage material.

2. Materials and methods
The materials used in this study were MgH₂ (99.99%, 50 μm size, Sigma Aldrich production), Ni (Hongwu Nano, 99%, 50 nm particle size), and silica carbide (SiC). These three reagents were combined and then split into two parts, namely MgH₂ + Ni + 5 wt.% SiC; and MgH₂ + Ni + 10 wt% SiC. Both parts then went through the milling process with three variations of time for 5, 10 and 15 h. The ratio of ball mills to samples is 10:1 and each process is carried out for 1 g of sample at 350 rpm.

3. Results and discussion
3.1. Phase identification results with X-Ray Diffraction (XRD)
Identification results using XRD for samples with five wt.% catalysts for three variations of the milling process times of 5 hours, 10 hours and 15 hours are shown in figure 1, while figure 2 shows the XRD results for ten wt.% catalysts. The phases in the sample can be identified by comparing experimental data with standard data published by the Joint Committee for Powder Diffraction Standards (JCPDS). The comparison results are shown in both figures (figure 1 and figure 2).

The result of the XRD pattern comparison indicate that the MgH₂ phase is the dominant phase at 2θ of 37.9° and 16.6° whereas the peak at 2θ of 35.6° belongs to Ni phase. The presence of the SiC phase is represented by the peaks at 2θ = 58.6° and 31.1°. The XRD results also indicate the presence of additional Mg(OD)₂ phases at 2θ = 50.7° and 18.4° which is estimated to be the result of oxidation that occurs during the weighing process until the transfer of samples to the milling container. The presence of this phase indicates that the material is contaminated with air so that the oxygen enters the sample.
Figure 2. XRD profile on MgH$_2$ + Ni + SiC material with a catalyst of 10 wt% SiC and three milling time variation of 5 hours, 10 hours and 15 hours.

This impurity may affect the hydrogen desorption process. Ni and SiC serve as a catalyst and is used in very small amounts, where the catalyst itself help to accelerate the reaction but actually does not react. That is why both the phases of the catalyst Ni and SiC are present in the XRD spectrum.

The width of the peaks of the XRD spectrum is represented by the FWHM value of each peak. The relatively similar shape and width of the diffraction spectra in figure 1 show that there is no significant change in the value of FWHM with the difference in milling process time. FWHM can also be used to get the crystal size from the sample using the Scherrer equation. The MgH$_2$ peaks from the samples with a 5% SiC catalyst have smaller FWHM value compared to a 10% SiC catalyst. Thus it can be said that the addition of the SiC catalyst decreases the crystal size of the sample. However, the XRD spectrum shows an increase in FWHM from the MgH$_2$ peaks by increasing the milling time of both the 5% and 10% SiC catalysts.

Ranjbar et al. [6] have found that silicon carbide (SiC) in addition to its role in the reactive milling process; it can also accelerate grain refinement due to the characteristics of the hard SiC as well as other carbide metals. The absorption capacity of hydrogen by MgH$_2$ network will increase with finer grain size since the hydrogen atoms can be easier when infiltrating to the hydrogen magnesium network. Furthermore, as reported by Ranjbar et al. [6] that the decrease in the grain size of the ductile Mg during the milling process of both Mg only or MgH$_2$ is also observed if the process is carried out in hydrogen environment. Furthermore, with its hardness characteristics, SiC also plays a role in reducing the size of the grain that makes the MgH$_2$ surface larger. The addition of this surface area will have a positive impact on the hydrogen desorption characteristics of MgH$_2$.

3.2. Surface morphological observation results with SEM

The surface morphology observation using SEM provides information that the grain dimensions for samples with a 10-hour milling time are smaller than grain dimensions for samples with a 5-hour milling time as shown in figure 3. However, as reported earlier by Ranjbar et al. [6] that during the milling process is believed that the hardness of Ni elements plays a role in reducing the grain size of MgH$_2$, so that its surface area becomes more substantial, which then affects the absorption and desorption of MgH$_2$. However, the amount of Ni catalysts in MgH$_2$ must also be limited, because excessive doping Ni will cause reduce the hydrogen absorption capacity, the reaction kinetics will be slow and can also hinder the hydrogen diffusion process [6].

3.3. Thermal investigation

Gravimetric testing using Thermogravimetric Analyzer (TGA) is required in studying hydrogen release capacity. Figure 4 shows the desorption behaviour of MgH$_2$ + Ni + 5wt% SiC with a milling process for 10 hours. These results indicate that the milling process for 10 hours can produce hydrogen...
Figure 3. The morphological structure of the sample MgH + Ni + 5 wt% SiC for (a) 5 hours and (b) 10 hours milling time

Figure 4. Desorption behaviour of MgH + Ni + 5wt% SiC with 10 hours of milling process.

as much as 12 wt.% in 16 minutes. These results correspond to Jalil et al. [10] which get smaller particle sizes can produce a larger contact surface area between the samples and hydrogen, which will increase hydrogen absorption rate.

4. Conclusions
From the results of the use of Ni and SiC catalysts on MgH, solid hydrogen storage material with two variations of wt.% SiC catalysts and three variations of milling time process, it can be concluded that the desorption properties of MgH, material can be improved, and both Ni and SiC catalysts are suitable catalysts.

Acknowledgements
Authors would like to express the gratitude to Andia Fatmaliana, M.Si. (PPs Unsyiah) who is responsible for XRD measurements.

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