Sorption behavior of MgH$_2$-Ti for Hydrogen storage material prepared by high pressure milling

Malahayati$^1$, Nurmalita$^2$, Ismail$^1$, M N Machmud$^3$ and Z Jalil$^{1,*}$

$^1$ Physics Department, Universitas Syiah Kuala, Banda Aceh, Indonesia
$^2$ Mechanical Engineering Department, Universitas Malikussaleh, Lhokseumawe, Indonesia
$^3$ Mechanical Engineering Department, Universitas Syiah Kuala, Banda Aceh, Indonesia

$^*$E-mail: zjalil@unsyiah.ac.id

Abstract. Synthesis by reactive ball milling under hydrogen atmosphere is a potential technology for preparation of hydrogen storage materials. In this report we proposed a high pressures reactive milling (hereafter referred as “HPRM”) for preparing the MgH$_2$-Ti. Nanocrystalline materials of MgH$_2$-Ti which is have been synthesized under high pressures hydrogen up to 9 MPa at room temperature. The characterization has been done by X-ray diffraction, scanning electron microscopy for their phase composition and morphology, respectively. Hydrogen storage capacities and the hydriding/dehydriding kinetics measured with gravimetric method. The X-ray diffraction pattern after 12 h of milling showed very broadened peaks, indicating that the crystal size was already in nanometers. It was also observed that the kinetics are fast which works within less than 7 mins for absorption (at 300$^\circ$C, 10 bar H$_2$) and within 6 mins for desorption (at 350$^\circ$C, 50 mbar H$_2$), respectively. The hydrogen storage capacity was 2.7 wt%.

1. Introduction
Magnesium based hydride is promising material for hydrogen storage application due to its lightweight, capacity, and low cost [1,2]. However, slow kinetics and high sorption temperature (> 300 $^\circ$C) have hindered its commercial use. Efforts have been proposed to make improvement in the hydriding and dehydriding characteristics such as element substitution [3], ball milling technique in preparation sample [4], and high-pressure treatment [5]. These results showed that the hydrogenation behavior was greatly changed, mainly due to the formation of nanocrystalline structure. Recently, new hydrides can also be successfully synthesized by using high pressure technology [6]. However, the work by mean milling metal hydrides under high hydrogen pressure is very rare. Some works showed that this experimental setup allowed the process to be run at hydrogen pressures at room temperature. Titanium (Ti) is an efficient catalyst, and Mg by addition Ti or TiH$_2$ showed one of the fastest kinetics for Mg-based materials. Mg-Ti and Mg-Ti-H systems have been investigated for metastable compounds with different thermodynamics property [7]. To prepare Mg-Ti nanostructured the most widely used composite and compound technique is ball milling and magnetron sputtering [8]. Motivated by this, in this work we
report the reactively milled of MgH\textsubscript{2}-Ti synthesized under high hydrogen pressure using a high energy planetary ball milling apparatus.

2. Materials and Method
In this work, pure MgH\textsubscript{2} powder (Goldsmith GmbH, 95+%), Ti (99.9%, Alfa Aesar) and purified hydrogen have been used. The mixing powders were filled into a milling vial and covered together with 14 balls. The ball diameter was 9.7 mm, and ball to powder ratio (BPR) was 10:1. The total amount of powder was 5 g (molar ratio 3:1). The planetary mill apparatus (Fritsch, P6) with a speed of 500 rpm was used. Periodically, after selected milling time, the milling process was stopped and refilled again with hydrogen. The milling pot is equipped with a valve to allow evacuation and gas filling. The vial was first evacuated for about 5 mins. After evacuation, a flow of hydrogen up to 9 MPa was filled carefully into the vial. A small amount of the powder was taken and stored in argon atmosphere glove box immediately after milling. The X-ray diffractometer analysis was carried out using Co-K\textsubscript{α} radiation and operated at 40 kV and 40 mA. Then, SEM micrograph (FEGSEM LEO 1530) was used for microstructural characterization. Finally, the hydrogen sorption properties were investigated by gravimetric sorption apparatus in a wide parameter range (1-10 bar, 50-300\textdegree C for absorption, 50 mbar-1 bar, 250-350\textdegree C for desorption).

3. Results and Discussion
The X-ray diffraction pattern showed the powders character from microcrystalline to nanocrystalline, with a milling time of up to 18 h (Fig.1). At the initial stage, the as received (before milling) and sample short milling (1 h) was showed mainly MgH\textsubscript{2} phase and a small peak of Ti (act as catalyst). Then, after 12 h milling times, the peak was getting broader. The broadening of the diffraction peaks is attributed to the reduction of the grain sizes of MgH\textsubscript{2}-Ti.

![Figure 1. XRD pattern of MgH\textsubscript{2}-Ti after various milling time.](image_url)

Furthermore, to follow the progress of the solid-gas reaction during milling elemental MgH\textsubscript{2}-Ti powder under high pressure hydrogen, the XRD analysis has been used. At the initial stage (before milling), the XRD pattern shows sharp peak corresponding to microcrystalline MgH\textsubscript{2} and Ti powder. After an hour of milling time, the elemental powders agglomerate [9] to form powder particles of greater diameters, as large as several hundred microns. But there are no changes in phase composition. It is also interested to note that the materials being nanocrystalline after 12 h (~ 10 nm) milling time. This can be explained
because of the high energy ball milling effect [10-14]. After 18 h, all the Bragg peaks corresponding to metallic Ti disappeared and a single phase of nanocrystalline MgH₂ appeared, indicated by the broader peaks.

The morphological changes of the powders during different HPRM time were followed by using SEM. The starting material has large particles of MgH₂. SEM micrographs show that the agglomerates have smooth surfaces and irregular shapes with size around tens microns. On the other hand, flaked MgH₂ particles undergone to the significant changes due to reactive milling (Fig. 2(b)). Worthy to note, after longer milling, the quantity of nano-size particles with sponge-like structure have been formed, but large agglomerates are still visible [15-18].

Figure 2. SEM images of MgH₂-Ti sample after milling. (a) 1 h, (b) 18 h.

Figure 3 shows the absorption mechanism of MgH₂-Ti after 18 h milling time. The hydrogen can reach ~ 2.7 wt% in capacity and proceed within 7 min at 300°C with at 10 bar. The capacity of hydrogen getting lower, when trying to process at 150°C. However, the kinetics are so fast, which can release hydrogen less than 6 min. It was reported that the storage capacity of hydrogen for the MgH₂ + 8 mol% Ti reached 2.6 wt% at 300°C within 15 min. Refer to this result, the increasing of destabilization effect on MgH₂ was Ti, Nb, Al, Fe, Ni and Cu, compared to the heat formation value of the mixtures [19]. Recently, Jangir et al showed that the Ti addition on MgH₂ has reduced the activation energy to various degree and it was found that the best result of MgH₂ by adding 10 wt% TiF₄ [20].

Figure 3. Absorption of MgH₂-Ti sample after milling 18 h.
Figure 4 shows, after desorption at 350°C, 50 mbar proceed within 6 minutes. Also, at 300°C, 275°C and 250°C desorption are proceed in 5, 6, and 8 minutes respectively. This also indicates that the desorption kinetics was fast. Although the gravimetric investigation showed that the hydrogen absorption was lower (~ 2.7 wt %) at 300°C, we can conclude that synthesis by mean high pressure reactive milling make the kinetics of MgH₂-Ti faster.

Conclusions
The reactive milling under high pressure of hydrogen in MgH$_2$ processing has been successfully done. High pressure milling of Ti added MgH$_2$ shows a significant effect on the sorption properties of Mg-based hydrogen storage material. Regarding the mechanism of hydrogen storage behavior, these results support the important factor of the catalysis of Ti incorporated in MgH$_2$ system. It was found the hydrogen reach ~ 2.7 wt% in capacity and is proceed within 6 minutes at 300°C with the pressure at 10 bar. The kinetics is very fast. However, the sorption temperature still high for the application purposes.

References
[1] Schlapbach L and Zuettel A 2001 Hydrogen storage materials for mobile applications, Nature 414
[2] Sellier D E, Aymoniera E, and Bobet J L 2009 Journal of Alloys and Compounds 476 152-159
[3] Barkhordarian G, Klassen T and Bormann R 2006 J. Phys. Chem. B 110 11020-11024.
[4] Song M Y, Kwon S N, Bae J-S and Hong S-H 2009 Journal of Alloys and Compounds 478 501-506.
[5] Oelerich W, Klassen T and Bormann R 2001 Mater. Trans. 42 1588-1592
[6] Choi Y J, Lu J, Sohn H Y, Fang Z Z 2008 Journal of Power Sources 180 491–497
[7] Zhang J, Sun L Q, Zhou Y C, Peng P 2015 Computational Materials Science 98 211-219
[8] Liang G, Shulz R 2003 Journal of Materials Science 38 6 1179-1184
[9] Jalil Z, Rahwanto A, Mulana F, Mustanjir 2016 International Journal of Technology 7 1301-1306
[10] Jalil Z, Rahwanto A, Handoko E, Mustanjir 2017 AIP Conference Proceedings 1826 020002.
[11] Malahayati, Ismail, Mursal, Jalil Z 2018 J. Phys.: Conf. Ser. 1120 012061
[12] Larsson P, Araujo C M, Larsson J A, Jena P and Ahuja R 2008 PNAS 105 8227–8231
[13] Pukazhselvan D, Sandhya K S, Ramasamy D, Shaula A and Fagg D F 2020 *Chem.Phys.Chem.* **21** 1-8

[14] Jalil Z, Rahwanto A, Sofyan H, Usman M and Handoko E 2018 *IOP Conf. Series: Earth and Environmental Science* **105** 012093

[15] Jalil Z, Rahwanto A, Akhyar H, Razali R and Handoko E 2018 *IOP Conf. Series: Earth and Environmental Science* **105** 012098

[16] Jalil Z, Rahwanto A, Ismail I, Sofyan H and Handoko E 2018 *Mater. Res. Express* **5** 064002

[17] Ismail I, Arliyani, Fathmiyah S, Mursal, Jalil Z and H P S A Khalil 2020 *Journal of Physics: Conference Series* **1572** 1

[18] Rahwanto A, Jalil Z, Akhyar, Handoko E 2020 *IOP Conf. Series: Materials Science and Engineering* **931** 012012

[19] Shang C X, Bououdina M, Song Y, Guo Z.X 2004 *International Journal of Hydrogen Energy* **29** 73-80

[20] Jangir M, Gattia D M, Peter A and Jain I P 2019 *AIP Conference Proceedings* **2145** 020006