NANOCRYSTALLINE MgH$_2$ FOR HYDROGEN STORAGE MATERIAL PREPARED BY MECHANICAL ALLOYING

Zulkarnain$^{1,2*}$, Muhammad$^1$, and O. Gutfleisch$^2$

$^1$Department of Physics, Syiah Kuala University, Darussalam, Banda Aceh 23111, INDONESIA
Phone/Fax.: +62-651- 7410516,
$^2$Leibniz Institute for Solid State and Materials Research, Helmholtzstr. 20, Dresden, Germany
*Corresponding author e-mail: zjalil@hfi.fisika.net

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ABSTRACT

In the future, hydrogen could potentially serve as a common clean energy source. A major barrier to its widespread use as a commercially viable fuel for vehicles is the lack of convenient and cost-effective hydrogen storage. Current hydrogen storage technologies rely on liquid and compressed gas systems. But, hydrogen can also be stored in various metals and intermetallic compounds called metal hydrides. Metal hydrides, however, are an alternative means for the compact and safe storage of hydrogen, by converting it into a dense solid form. Here, we report the structural investigation of nanocrystalline materials MgH$_2$ + 1 wt% Fe which milled using intensive mechanical milling process with the various milling time up to 80 hours.

Keywords: magnesium, metal hydrides, hydrogen storage

1. INTRODUCTION

The interest in hydrogen as an energy carrier has increased considerably during the last decades, but there are still many unsolved problems that have to be addressed before hydrogen can be implemented into today's infrastructure. One of these problems is storing the hydrogen. Today, hydrogen is stored as a compressed gas for example in vehicles, or a cryogenic liquid in physical storage systems for transport. Hydrogen can also be stored in various metals and intermetallic compounds called metal hydrides. Metal hydrides, however, are an alternative means for the compact and safe storage of hydrogen, by converting it into a dense solid form.

Work is being done on finding cheaper metal alloys which have the ability to absorb large amounts of hydrogen, and at the same time release the hydrogen at a relatively low temperature. Among the different hydrogen storage materials, Mg-based metal hydrides are promising candidates for reversible hydrogen storage because of their high capacity, lightweight, and low cost$^1$. However, relatively high sorption temperatures (>300°C) and low kinetics are the major difficulties hindering its commercial use. This high temperature is mostly due to the high enthalpy (-76 kJ/mol). Recent effort has been done to improve the hydriding and dehydriding properties using techniques such as element substitution, ball milling technique, and high pressure treatment$^{2-4}$. These results showed that the hydrgenation behavior was greatly changed, mainly due to the formation of nanocrystallines structure.

Motivated by this, here we report the high energy ball milled of MgH$_2$+1wt% Fe milled under argon atmosphere. We use ball milling facility to improve the kinetics of Mg-based hydrides. Usually takes a long time to prepare alloy by MA method and the sample can be contaminated during the milling process. This type of milling has improved hydrogen sorption characteristics of Mg-based hydrides.

2. MATERIALS AND METHODS

Pure MgH$_2$ powder (from Goldschmidt GmbH, 95+%), Fe (99.9%, Johnson Matthey) and purified hydrogen have been used. The powders were filled into a hardened steel vial and sealed together with 13 balls (9.5 mm in diameter). The total amount of powder was 5 g with a ball to powder weight ratio of 10 : 1. All this operations were performed in glove box under argon atmosphere to prevent oxidation. The Retsch PM400 planetary mill apparatus was used with a rotational speed of 200 rpm and the various milling times of 2, 4, 10, 20, 40, 60, and 80 h. After selected milling time, a small amount of powder were immediately taken and stored in argon atmosphere glove box in order to avoid from the oxygen contamination.

The X-ray powder diffraction analysis was carried out by Philips 1050 diffractometer using Co-K$\alpha$ radiation.
operating at 40 kV and 40 mA, measuring region 20\(^\circ\)–110\(^\circ\), step width \(\Delta\theta\) 0.05\(^\circ\), and measuring time per step, 8 second. The microstructural characterization were investigated by using SEM (FEGSEM LEO 1530).

3. RESULTS AND DISCUSSION

Figure 1 shows the evolution of the XRD diffraction pattern for MgH\(_2\)-1wt%Fe as a function milling time. The starting mixture shows the presence of microcrystalline magnesium hydride, MgH\(_2\) and iron. It can be seen that during milling the MgH\(_2\) and Fe diffraction peaks broaden but no changes in the 20 position. The as-received sample composed mainly MgH\(_2\) and a small peak of Fe at 20 = 52.55\(^\circ\). The MgH\(_2\) peak appears at 20 = 32.75\(^\circ\), 42.05\(^\circ\), 61.66\(^\circ\), 68.24\(^\circ\), 77.73\(^\circ\), 81.85\(^\circ\), 83.23\(^\circ\), 90.93\(^\circ\), 101.39\(^\circ\). The peak width increases with the increasing of milling time. Then, after 10 h milling the peaks are broader, and during 20 h of milling the metastable \(\gamma\)-MgH2 peaks appears at 20 = 30.22\(^\circ\). For prolonged milling times, the concentration of MgH2 and iron increases. But the phase formation shows that no changes in phase composition.

An interesting result is that the X-ray diffraction pattern after 80 h milling times are extremely broader. This indicate that the crystallite size getting nanometer (~10 nm). This result also shows that mechanical alloying as one of effective technique in preparing the nanocrystalline materials, especially for hydrogen storage materials which needed small size particles in order to get the highest hydrogen capacity. Figure 2 pointed out the schematic of ball motion inside the ball mill apparatus in a planetary ball mill. These are arranged on a rotating support disk and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the vials rotating around their own axes and that produced by the rotating support disk both act on the vial contents, consisting of material to be ground and the grinding balls. Since the vials and the supporting disk rotate in opposite directions, the centrifugal forces alternately act in like and opposite directions. This causes the grinding balls to run down the inside wall of the vial named the friction effect, followed by the material being ground and grinding balls lifting of and traveling freely through the inner chamber of the vial and colliding against the opposing inside wall as the impact effect\(^5\).

**Fig. 1.** X-ray diffraction pattern of MgH\(_2\)-1 wt% Fe as function milling time.

**Fig. 2.** Schematic the ball motion inside the ball mill apparatus\(^5\).
Yuan et al.\textsuperscript{6} reported that there is a correlation between mechanical ball milling and the hydrogen sorption properties of hydrogen storage materials (in their case, LaMg\textsubscript{11}Ni). There is a 20 % increase of hydrogen absorption capacity after 20 h milling and the kinetics of hydrogen absorption was improved. They also pointed out, when the milling time is too long, the situation will be deteriorated.

Fig. 3. SEM images of MgH\textsubscript{2}-1wt% Fe before milling (a) and after several milling times; 4 h (b), 8 h (c), 80 h (d).

Figure 3 shows some SEM images of the sample powder before and after several hours of milling times. The surface of the powders is very irregular, as a result of the repeated fracturing events during the milling process. In this work, Fe acts as catalyst which used only in small amount, 1 wt%. When magnesium was subjected to ball-milling without any additives, the magnesium was not formed in a finely divided form\textsuperscript{7}. Confirmation of the morphological changes produced by intensive ball milling can be seen that the particles of the powder before milling is large, still in microcrystallite size around 100 µm and mainly performed on ductile Mg (Fig. 3a). Then, after longer milling times the morphology of the samples are getting difference in size. Especially, after 80h of milling the crystallite size already in nanometer size.

4. CONCLUSIONS

Preparation and structural characterization of nanocrystalline magnesium were studied by using MgH\textsubscript{2} catalyzed with small amount of Fe (1 wt%). It showed that after 80 hours of milling time the crystallite size decreases around tens nanometer. This can be noted that the intensive mechanical alloying showed an interesting way to synthesize the magnesium based hydrogen storage material. After 20 h the metastable γ-MgH\textsubscript{2} peaks appears at 2θ = 30.22°, and for prolonged milling times, the concentration of MgH\textsubscript{2} and iron increases. But there is no changes in the phase composition. On the basis of these results, we will observe the hydrogen sorption properties of the material.

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REFERENCES


