Effect of nanostructure Ni on the sorption properties of mechanical milled MgH2 for solid hydrogen storage materials

by Erfan Handoko
Effect of nanostructure Ni on the sorption properties of mechanical milled MgH₂ for solid hydrogen storage materials

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Abstract. Among the metal hydrides, magnesium has the theoretically highest weight capacity for hydrogen storage (7.6 wt.%), lightweight and a reasonably low cost. However, high working temperature (≥300°C), slow reaction kinetics (need more than 1 hour to produce 5 wt% of hydrogen) and difficult activation limit the practical application of Mg-based hydrides. In order to improve their performance, MgH₂ was catalyzed with Ni nanoparticles which reactively milled under hydrogen atmosphere. Phase identification and microstructure were characterized by XRD and scanning electron microscope (SEM). Hydrogen sorption properties were studied by gravimetric analysis method. The results show that, small amount of Ni in nanometer scale proved to be as a suitable catalyst for improvement the kinetics of MgH₂ and at the same time allowed to reduce the milling time process.

1 Introduction

Among the metal hydrides, magnesium has the theoretically highest weight capacity for hydrogen storage (7.6 wt.%), lightweight and a reasonably low cost [1]. However, high working temperature (≥300°C), slow reaction kinetics (need more than 1 hour to produce 5 wt% of hydrogen) and difficult activation limit the practical application of Mg-based hydrides. Many efforts have been done to improve the hydrating and dehydrating properties such as element substitution (metal or metal oxides) as catalyst in nanometer scale and modification of ball milling technique have been used to improve sorption and kinetics properties [2-4]. Recently, the reactive ball milling under hydrogen atmosphere was successfully introduced to prepare hydrogen storage materials [5-8]. Here, we report on MgH₂ catalyzed with small amount of Ni in nanoparticles scale and the preparation was done by reactive ball milling under 10 bar hydrogen.

2 Materials and Method

MgH₂ (Goldschmidt, 95.4%), Ni (99.9%, Sigma Aldrich, ~90 nm) powders were used to prepare the samples. The powders were filled into a hardened steel vial and sealed together with 13 balls (9.5 mm in diameter) and reactively milled in a planetary mill Fritsch (P6) at a rotational speed of 400 rpm (ball to powder ratio 10:1) for 2 hours under hydrogen atmosphere (10 bar). Phase identification and microstructure were characterized by XRD using a Philips 1050 diffractometer (Cu-Kα radiation) and scanning electron microscope (FEGSEM LEO 1530). Hydrogen sorption properties were studied by gravimetric analysis in a wide temperature range for absorption (50-300 °C) and desorption (250-350 °C).

3 Results and Discussion

Figure 1 shows the evolution of the XRD diffraction pattern as a function of milling time. The starting mixture of MgH₂-2 mol% nano-Ni shows the presence of microcrystalline magnesium hydride and Ni nanoparticles. It can be seen that during milling the MgH₂ and Ni diffraction peaks broaden but no changes in the 2θ position at early stage of milling. The as-received sample composed mainly MgH₂ and a small peak of Ni. The same result found after 1 h milling. Then after 2 hour of milling the peaks are broader. It can be also note that after desorption hydrogen completely react to produce only magnesium. We can conclude that MgH₂ completely desorp after milling only two hours.

Fig. 1. XRD patterns of MgH₂-2 mol% nano-Ni reactively milled for 2 hours.
It was also observed that with increasing milling time the crystallite sizes decrease further to finally stabilize around tens nanometer. Thus, making use of hydrogen pressure during milling promotes the formation of larger amounts of MgH₂ [9-11].

The hydrogen storage and release properties of Ni-catalyzed MgH₂ were measured by gravimetric method. The gravimetric analysis measurements confirm the catalytic effect of nickel nanoparticle on magnesium hydride hydrogenation and dehydrogenation. Figure 2 shows the hydrogen absorption curves of MgH₂-2mol% Ni nanoparticles compared to microparticles and pure MgH₂ samples as well at constant temperatures (300°C) and pressures (10 bar) after reactive ball milling under 10 bar H₂ for 2 hours.

![Graph showing hydrogen absorption curves](image)

**Fig. 2.** Hydrogen absorption of of MgH₂-2 mol% nano-Ni reactively milled for 2 hours in 10 bar H₂ reactive milling under 10 bar H₂.

The catalytic effect of nickel nanoparticles is magnified especially during absorption; actually, the absorption in the sample catalyzed with Ni nanoparticles took less than 5 minutes for uptake 5.3 wt% H₂. Compare to the sample catalyzed with Ni microparticles took more than 60 minutes to absorb 5.3 wt% of hydrogen, and the same result for pure MgH₂ as well.

The results show that the Ni catalyst absorbs large amount of hydrogen for short time in the form of nanoparticles. And the large particle catalyst requires a longer time to finish the absorption. It is obvious that Ni has much better as catalyst in nanoparticle size in the absorption and desorption processes. This is also one reason for the great interest in the use of nanoparticles catalyst in order to improve the hydrogen sorption properties of MgH₂. However, the effect of Ni nanoparticles has no effect on the operation temperature which needed high temperature, more than 300°C, to complete the absorption.

![Graph showing hydrogen desorption curves](image)

**Fig. 3.** Hydrogen desorption of of MgH₂-2 mol% nano-Ni reactively milled for 2 hours in 10 bar H₂ reactive milling under 10 bar H₂.

Similar to desorption, its need 350°C to desorp 5.3 wt% of hydrogen as shown in Fig 3. But, the kinetics of absorption/desorption was extremely fast, which work only in 5 minutes. As can be seen clearly, the addition of metal nanoparticles leads to a notable enhancement of both the absorption and desorption kinetics. In this case, it can be concluded that this enhancement in the hydrogen sorption kinetics properties is due to the presence of Ni nanoparticle as a catalyst in MgH₂ and the high pressure of milling as well.

A fundamental study of the role of catalysts in MgH₂ nanoclusters was provided by carrying out based on density functional theory [12]. Interesting to note that the diffusion mechanism may account for the fact that a small amount of catalysts is sufficient in improving the MgH₂ kinetics, which is essential for the use of this material for hydrogen storage application.

The SEM micrographs of Fig. 4 show secondary electron image of powders reactively milled in the planetary mill for 2h (a) and 2h (b). The areas with the white contrast (Mg) disappear with increasing milling time leading to improved homogeneity. The surface of the powder is irregular, as a result of the fracturing during the milling process [13,14]. From the SEM data inform that at the early milling time, the sample has particle size about 20 μm. Then, after milling the sample has been reduced until 1 μm.
4 Conclusions

MgH₂ catalyzed with small amount of nano-Ni as catalyst has been prepared via reactive milling. This high energy planetary ball mil (HEPBMI) produced a high surface area powders and showed the nano-Ni particles dispersed on the surface of Mg uniformly. The MgH₂-2mol% Ni nanopowders exhibited the sorption kinetics properties, absorb/desorb 5.3 wt% of hydrogen within 5 minutes. It is also clear that, the use of nanopowder Ni and reactive milling method are very effective to reduce the milling process in short time.

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References

1. Schlappbach and Zueettel, Hydrogen storage materials for mobile applications. Nature. Vol 414, 15 November (2001)
2. Sandrock, G. & Thomas, G., The IEA/DOE/SNL on-line hydride databases. Appl. Phys. A 72, 153–155 (2001)
3. H. Imamura, Y. Maruta, S. Tsuehiya, Magnesium-based hydrogen-storage materials: Solvated Mg-Ni by metal vapour deposition, J. Less-Common Met. 135, 277. (1987)
4. Myong Youp Song, Sung Nam Kwon, Jong-Soo Bae and Seong-Hyoun Hong, Hydrogen-storage properties of melt spun Mg-23.5 wt%Ni milled with nano Nb₂O₅, Journal of Alloys and Compounds, 478, 501-506 (2009)
5. H. Yuan, Y. An, G. Xu, C. Chen, Hydriding behavior of magnesium-based hydrogen storage alloy modified by mechanical ball-milling, Mater. Chem. Phys., 83, 340. (2004)
6. J. Hoot, J.F. Pelletier, G. Liang, M. Sutton, R. Schulz, Structure of nanocomposite metal hydrides, J. of Alloys and Compounds 330-332, 727-731. (2002)
7. M. S. El-Eskandarany, E. Shaban, N. Ali, F. Aldakheel, A. Alkandary, In-situ catalyzation approach for enhancing the hydrogenation/dehydrogenation kinetics of MgH₂ powders with Ni particles, Sci. Rep. 6, 37335. (2016)
8. J.-L. Bobet, E. Akiba, Y. Nakamura, B. Darriet, Study of Mg-M (M = Co, Ni, and Fe) mixture elaborated by reactive mechanical alloying, International Journal of Hydrogen Energy 25, 987-996. (2000)
9. Z. Jalil, A. Rahwanto, F. Mulana, Mustanir, International Journal of Technology, 7(8), 1301-1306. (2016).
10. Z. Jalil, A. Rahwanto, E. Handoko, Mustanir, AIP Conference Proceedings 1826 (1), 020002, (2017)
11. Z. Jalil, A. Rahwanto, Mustanir, Akhyar, E. Handoko, AIP Conference Proceedings 1862, 030023. (2017)
12. Peter Larsson, C. Myles Arrijo, J. Andreas Larsson, Prat Jena, and Rajeev Ahuja, Role of catalysts in dehydrogenation of MgH₂ nanoclusters, PNAS June 17, 2008 vol. 105 no. 24 8227-8231. (2008)
13. Z. Jalil, A. Rahwanto, H. Soñin, M. Usman and E. Handoko. The use of Silica from beach sand as catalyst in Magnesium-based hydrides for Hydrogen storage materials. IOP Conf. Series: Earth and Environmental Science 105, 012093. (2018)
14. Z. Jalil, A. Rahwanto, H. Akhyar, R. Razali and E. Handoko, MgH₂-SiC based hydrogen storage material prepared by reactive mechanical alloying method, IOP Conf. Series: Earth and Environmental Science 105, 012098. (2018)
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**PRIMARY SOURCES**

1. M. Herrich, N. Ismail, J. Lyubina, A. Handstein, A. Pratt, O. Gutfleisch. "Synthesis and decomposition of Mg2FeH6 prepared by reactive milling", Materials Science and Engineering: B, 2004

2. Oelerich, W.. "Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials", Journal of Alloys and Compounds, 20010209

3. "Simple Metal and Intermetallic Hydrides", Fuel Cells and Hydrogen Energy, 2009

4. Puszkiel, J.A.. "Hydrogen storage properties of Mg"xFe (x: 2, 3 and 15) compounds produced by reactive ball milling", Journal of Power Sources, 20090101
| Reference | Author(s) | Title | Publication |
|-----------|-----------|-------|-------------|
| 5 | Haizhen Liu, Xinhua Wang, Yongan Liu, Zhaohui Dong, Hongwei Ge, Shouquan Li, Mi Yan | "Hydrogen Desorption Properties of the MgH –AlH Composites" | The Journal of Physical Chemistry C, 2013 |
| 6 | | | ieahia.org |
| 7 | Suryanarayana, C., and Nasser Al-Aqeeli | "Mechanically alloyed nanocomposites" | Progress in Materials Science, 2013 |
| 8 | Yim, C.D. | "Hydriding properties of Mg-xNi alloys with different microstructures" | Catalysis Today, 20070228 |
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