MgH$_2$-SiC based hydrogen storage material prepared by reactive mechanical alloying method

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Abstract. Hydrogen storage in metal hydrides, compared to conventional methods, is regarded as one of the best solutions due to the higher volumetric storage capacity and safety. Magnesium and magnesium-based alloys are promising candidates for hydrogen storage. The hydrogen storage capacity of magnesium in the form of MgH$_2$ amounts to 7.6 wt%. Unfortunately, Mg has a high thermodynamic stability and therefore, relatively slow desorption kinetics, which are the major drawbacks for the application as a hydrogen storage material. Various techniques are developed to improve the sorption characteristics by accelerating the aforesaid processes. In this work we success to synthesis and investigate the catalytic effect of SiC and Ni (in nanostructure scale) on MgH$_2$ using reactive mechanical alloying method in 10 bar H$_2$. At first step, using SiC catalyst the sorption properties can be improved. The most promising step by using double catalysts of SiC and Ni (MgH$_2$-5wt%SiC-5wt%Ni) which absorb 5.7 wt% hydrogen and at the same time decrease the desorption temperature to 250°C. Compared to T onset of pure MgH$_2$-which desorp at 380°C. To the best of our knowledge, this is the best result so far for MgH$_2$-SiC system.

1. Introduction

Presently, metal hydrides are the most promising materials for hydrogen storage, especially the lightweight metal alloy hydrides. The research is focused now on the new lightweight materials for hydrogen storage. Magnesium (Mg) is considered to be the most promising base material; it forms MgH$_2$ which corresponds to a hydrogen content of 7.6 wt% [1, 2]. Some efforts have been done in order to enhance the hydrogen absorption rate and to overcome the problems connected with the high absorption/desorption temperatures by alloying Mg/MgH$_2$ with other metals.

Some studies are devoted to the catalytic effect of 3d-transition metals, especially the Ni metal [3-7]. Recently, Eskandarany et al. [7] have showed a new approach for catalyzing MgH$_2$ with nano-Ni by high energy reactive ball milling under 50 bar of hydrogen atmosphere. They found that the sorption kinetics was examined at 275 °C within 8 minutes and produced ~5 wt.% H$_2$ for 25 h of milling time.
In this work we make attention on the effect dual catalyst of nano-Ni and SiC on the hydrogen storage properties of MgH₂ and prepared by mechanical milling in “mild” condition with relatively low hydrogen pressure (10 bar) for 2 hours.

2. Materials and Method
The pure MgH₂ powder (Sigma Aldrich, 99.99%, 50 µm) and Ni nanopowder (Sigma Aldrich, 99.9%, 90 nm) and SiC (Hongwu Nano, 50 nm, 99%) were used. Hardened steel crucibles of 9.5 mm in diameter containing 13 balls were filled; the total amount of powder was 5 g with a ball to powder weight ratio of 10:1. The Fritsch P6 planetary mill apparatus attached with a home-made reactive milling vial was used with a rotation speed of 200 rpm and with the milling times of 2h in 10 bar of hydrogen atmosphere.

The X-ray powder diffraction analysis after different milling was carried out by Philips PW3710 diffractometer using Co-Kα radiation, operating at 40 kV and 40 mA. The microstructural characterization were investigated by using SEM (JEOL JSM-5310LV). The hydrogen storage properties were investigated by gravimetric method in a wide temperature and pressure range for absorption (1-10 bar, 50-300 °C) and desorption (250-350 °C, 50 mbar-1 bar).

3. Results and Discussion
Figure 1 shows the evolution of X ray diffraction patterns for MgH₂-5wt% SiC-5wt% Ni material as a function of milling time and intensity. At the time of mixing the material is still in the pre-milling phase it is clear that the MgH₂ phase appears as the main phase at the angle of 2θ = 32.75°, 42.05°, 61.66°, 68.24°, 77.73°, 81.85°, 83.23°, 90.93°, 101.39°.

![Figure 1. XRD pattern of the samples MgH₂-5wt%SiC-5wt%Ni](image)

When milling lasts for 15-45 minutes, the form of diffraction pattern has not yet shown a significant change. Here it is known that crystal size is still microcrystalline. Different situations are shown on milling for 10 hours, where diffraction peaks begin to widen. It can be mentioned that at a time of 10 hours of milling, material begins to reduce grain size. Interestingly note that the smoothing
process lasts relatively short (10 hours). Compared to non-reactive processes, it looks less effective in terms of production time.

In this study directly used commercial MgH$_2$ material. Referring to the literature, the use of MgH$_2$ material directly in the study, compared to pure Mg, would be able to obtain a nanocrystal structured material with a higher surface area which would affect the kinetics during the hydriding process [8]. Particle size particle size distribution of MgH$_2$-5wt% SiC-5wt% Ni (10 hours RMA) observed with particle size analyzer (PSA) indicates that grain size decreases as smoothness increases. From the measurement results it is known that the average size of particles is 0.6-0.28 μm, smoother than without the milling process. Reported by Varin et al [9] that increasingly decreasing particles will form an increasingly larger surface area so the atoms of H will easily recombine. This will have a strong effect on the change in the properties of MgH$_2$ uptake.

Revezs et al [10] uses the convolutional model of multiple whole profile fitting procedure (CMWP) to analyze the XRD peak profiles. Obtained information that fine grain has a large contribution to the absorption and desorption of MgH$_2$ material.

The surface of the powder are irregular, as a result of the fracturing during the milling process. The SEM image after 2 hours of milling shown the finer powder. It seem the powder was already in nanocrystal scale. If we compare with XRD, this is consistent with the structural analysis by XRD. After calculated by Scherrer method [13], the particles were reaches around tens nanometer after 2 h of reactive milling. The silicon carbide in the composites helps to break the magnesium particles into smaller sizes due to its hardness. addition of SiC can help to generate smaller MgH2 nanocrystals and it was found that the MgH$_2$ peaks in the XRD pattern became very broadened.

It appears that the pure MgH$_2$ (T onset) temperature of the pure MgH$_2$ is around 380°C. This result corresponds to reference which indicates that the high temperature MgH$_2$ operation. Then, the attempt to lower the onset was done by adding 5wt% SiC to the sample MgH$_2$-5wt% SiC. The onset showed a decrease compared to MgH$_2$, where it was decomposed at 350°C. Referring to Ranjbar et al [12] report, the result obtained indicates the suitability.

Furthermore, the addition of SiC and Ni nanoparticle catalysts (MgH$_2$-5wt% SiC-5wt% Ni) showed a significant decrease in temperature of desorption, whereas T onset could be reduced to 250°C. Suspected that the addition of nano-structured Ni catalysts could affect material performance based on MgH$_2$-SiC.

The observed attraction is the presence of Ni nanoparticle catalysts that affect the decrease of MgH$_2$ desorption temperature. Specifically, Xiea et al [11] studied the kinetics of MgH$_2$ desorption that increased dramatically by nanoparticle doping. However, the desorption kinetics do not increase as the Ni catalysts exceed a certain value.
By comparing the structure, particle size and configuration of the catalyst obtained, it can be demonstrated that the desorption kinetics can be improved, mainly due to the combination of atomic hydrogen acceleration on MgH$_2$ surface by Ni nanoparticles. Xiea believes that the size of the catalyst particles is beneficial to increase the catalytic effect and at the same time hydrogen storage capacity can still be maintained.

The amount of Ni catalyst in the material is also considered. When the amount of catalyst is too large it will lower the capacity of the hydrogen that can be absorbed. According to Xiea, the use of up to 25% catalysts can lower the onset of MgH$_2$, but if usage exceeds 25% then the onset T does not change, while H$_2$ capacity decreases. On the other hand, minimize Ni catalyst particle size also affects MgH$_2$ performance.

4. Conclusion
Preparation and structural characterization of magnesium-based material, in this case MgH$_2$ with addition of 5wt% of SiC and Ni double catalysts have been successfully applied using reactive mechanical alloying (RMA) preparation using hydrogen at 10 bar pressure. XRD observation results show that the MgH$_2$:5wt% SiC:5wt% Ni nanoparticles coated for 10 hours form the main phase of MgH$_2$. The addition of SiC and Ni nanoparticle catalysts (MgH$_2$:5wt% SiC:5wt% Ni) showed a significant decrease in temperature of desorption, where $T_{onset}$ was reduced to 250$^\circ$ C. This result succeeded in repairing a pure MgH$_2$ T$_{onset}$ which reached 380$^\circ$ C. Although operational temperature was still relative high mass applications, reactive mechanical alloying techniques and the addition of double catalysts (SiC, Ni) to MgH$_2$ material promising for magnesium-based hydrogen storage R & D materials.
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