

# NB<sub>2</sub>O<sub>5</sub> AND SI ENHANCED HYDROGEN SORPTION KINETICS SYNTHESIZED BY MECHANICAL MILLING

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## ABSTRACT

In this paper, the hydrogen sorption kinetics and destabilization of thermodynamics of MgH<sub>2</sub> with addition of niobium pentoxide and silicon as additives have been studied. It was reported that, milling MgH<sub>2</sub> with additives, specifically with Nb<sub>2</sub>O<sub>5</sub> improves the hydrogen sorption kinetics meanwhile Si destabilizes the thermodynamic by reducing the enthalpy of reaction. Mg-based element is a promising one because of the high hydrogen capacity with 7.6 mass%, low cost and rich in natural resources. However, improvement in de/hydrogenation kinetics and high desorption temperature of MgH<sub>2</sub> is required for hydrogen energy application.

A series of experiments with different amount of catalysts composition was performed. Hydrogen storage alloys were prepared from pure MgH<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>-Si by mechanical milling using a Fritsch P7 planetary ball mill for 20 hours. Samples were prepared with 300 rpm of rotational speed under a high purity Ar atmosphere with balls to powder mass ratio of 10:1. The phase structures, desorption behavior and particles morphology were determined by XRD, DSC and SEM respectively. Sievert type apparatus was also used to examine the hydrogen storage properties of the milled samples.

Commercial MgH<sub>2</sub> and MgH<sub>2</sub> milled with each catalyst were used as reference materials for investigating the catalytic effect on MgH<sub>2</sub> behavior. The results revealed that H<sub>2</sub> absorption kinetics were significantly improved with addition of Nb<sub>2</sub>O<sub>5</sub> and Si as compared to pure milled MgH<sub>2</sub>. However, the interaction between Nb<sub>2</sub>O<sub>5</sub> and Si seemed to be ambiguous as the kinetics became slower for samples with multiple additives. Hydrogen desorption temperature decreased in all investigated samples particularly for MgH<sub>2</sub>+10wt%Nb<sub>2</sub>O<sub>5</sub> with

the smallest value of activation energy of 29 kJ/mol. The dehydrogenated samples showed decreased enthalpy value in hydrogen desorption behavior. The additives had been shown to improve both H<sub>2</sub> absorption kinetics and destabilization of thermodynamics.

## 1. INTRODUCTION

Hydrogen storage is one of the greatest challenges for application of hydrogen energy for today's technology. MgH<sub>2</sub> is one of the most studied materials for hydrogen storage in the solid state as MgH<sub>2</sub> has a high hydrogen capacity of 7.6 wt%. Magnesium hydride has received a lot of attention as a reversible hydrogen storage material because Mg-based element is rich in natural resources and can be obtained at low cost. However, magnesium hydride has a weakness of slow de/hydrogenation kinetics, apart from having extremely high desorption temperature around 370°C due to its high thermodynamic stability.

An improvement in the hydrogen sorption and destabilization of thermodynamics are required in order to improve the characteristics of magnesium hydride for hydrogen energy application. A significant improvement in hydrogen sorption has been achieved recently by milling nanocrystalline MgH<sub>2</sub> with catalysts, which consist of niobium pentoxide and silicon.

In the present work, we focused on the effect of catalysts on the improvement of sorption kinetics by destabilization of MgH<sub>2</sub>. The samples were prepared by using a mechanical milling process to examine the catalytic effects on MgH<sub>2</sub>. The catalysts were added in order to decrease the hydrogen desorption temperature as well as to improve the sorption kinetics of MgH<sub>2</sub>.

## 2. EXPERIMENTAL

A series of experiments with different amounts of catalysts composition was performed from the mixture of powder magnesium hydride, MgH<sub>2</sub> (NaBiCo Biocoke Laboratory, 98% purity) with a mean particle of approximately 60 μm in size, niobium pentoxide, Nb<sub>2</sub>O<sub>5</sub> (Furuuchi Chemical Corporation, <149 μm, 99.9% purity) and silicon, Si (Furuuchi Chemical Corporation, <149 μm, 99.99% purity). Mechanical milling was carried out by a Fritsch P7 planetary ball mill for 20 h at rotational speed of 300 rpm and the ball to mass powder ratio was set up to 10:1. Hydrogen storage alloys using MgH<sub>2</sub> milled with catalysts were set to 90wt%MgH<sub>2</sub>+Xwt%Nb<sub>2</sub>O<sub>5</sub>+Ywt%Si with X:Y=10:0, 7.5:2.5, 5:5, 2.5:7.5, 0:10 respectively.

X-ray diffraction (XRD) patterns were obtained from ball-milled powders using X-ray diffractometer, XRD; Rigaku ULTIMA IV operating at a scanning speed of 2 deg/min and in-steps of 0.02° with Cu K $\alpha$  radiation. The thermal analysis of the materials was carried out by a differential scanning calorimeter (DSC; Shimadzu DSC-60) at several heating rate of 5, 10, 15 and 20 °C/min, and the mass of the samples was measured to 5 mg. DSC test was done under a high-purity argon gas flow (50 mL/min) to prevent the samples oxidization. The morphology of the powders was observed by a scanning electron microscope (SEM), JEOL10-60LV. The hydrogen absorption kinetics was evaluated by using a volumetric Sievert apparatus (Japan Metals & Chemical Co. Ltd.) at 300°C, and the mass of each measurement was about 200 mg. The samples were dehydrided for 20 h in vacuum prior to the activation of Mg. The absorption kinetics was recorded at a hydrogen pressure of 1 MPa.

## 3. RESULTS & DISCUSSION

The XRD patterns of materials after ball milling are presented in Fig.1. After 20 h of milling under argon gas, the diffraction peaks of low pressure tetragonal  $\beta$ -MgH<sub>2</sub> were broaden for all samples. This indicates that the samples underwent high energy ball milling during mechanical milling processes, which had led to a decrease in crystallite size (nanograins) within the powder particles. Consequently, there was a significant increase in specific surface area which then had contributed to the sorption kinetics after being milled for 20 h. Marek et al. [3] had reported formation of crystallite size, which may be accompanied by the introduction of lattice strain as well.

Nevertheless, no peaks of high pressure orthorhombic  $\gamma$ -MgH<sub>2</sub> was seen in all samples after mechanical milling process. Gennari et al. [4] reported 35 to 100 h of milling time is needed for the presence of  $\gamma$ -MgH<sub>2</sub> in crystalline structure, and it

was suggested that  $\gamma$ -MgH<sub>2</sub> phase appeared after hydrogenation process as high pressure of hydrogen gas was applied during absorption kinetics evaluation.

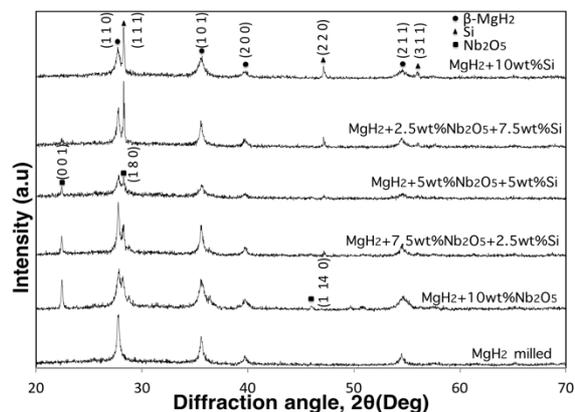


Fig. 1 XRD patterns of MgH<sub>2</sub> after ball milling for 20 h with and without addition of catalysts.

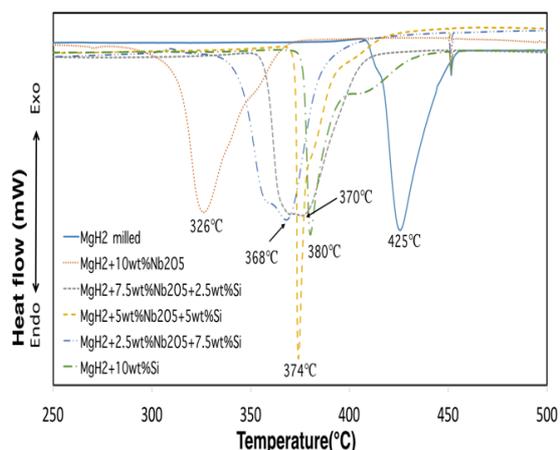


Fig. 2 DSC curves of MgH<sub>2</sub> without and with addition of different amount of Nb<sub>2</sub>O<sub>5</sub> and Si at heating rate of 5 °C/min.

DSC results confirm that improvement on hydrogen desorption behavior was achieved after addition of Nb<sub>2</sub>O<sub>5</sub> and Si, as shown in Fig. 2. It shows that the hydrogen desorption temperature shifted to lower temperature in all samples milled with catalysts. This suggests that the substantial increase in surface area due to the decrease in particles size during ball milling processes reduced the hydrogen desorption temperature significantly. Moreover, addition of Nb<sub>2</sub>O<sub>5</sub> might lead to the decrease in hydrogen desorption temperature as reported by A. Patah et al. [1]. Meanwhile, Bystrzycki et al. reported that Si had enhanced the improvement in desorption temperature by reducing the enthalpy value needed during desorption of hydrogen. MgH<sub>2</sub>+10wt%Nb<sub>2</sub>O<sub>5</sub> showed the lowest hydrogen desorption temperature (326°C) among all investigated samples with the smallest value of activation energy of 29 kJ/mol.

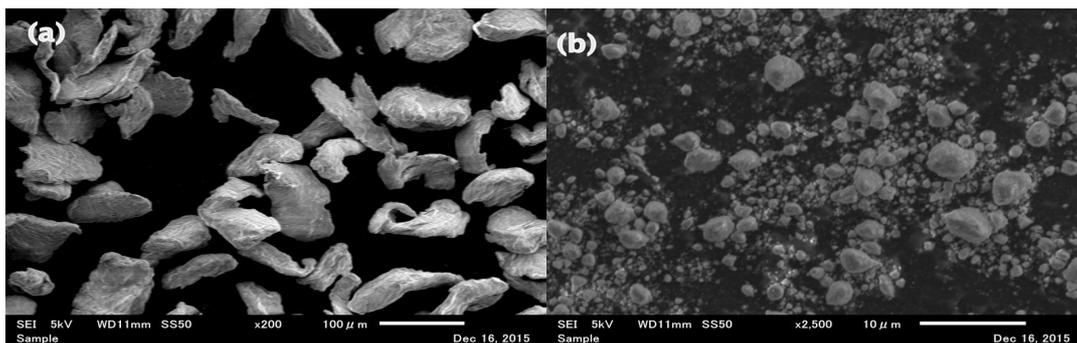


Fig. 3 SEM micrographs of MgH<sub>2</sub> (a) before and (b) after mechanical milling for 20 h.

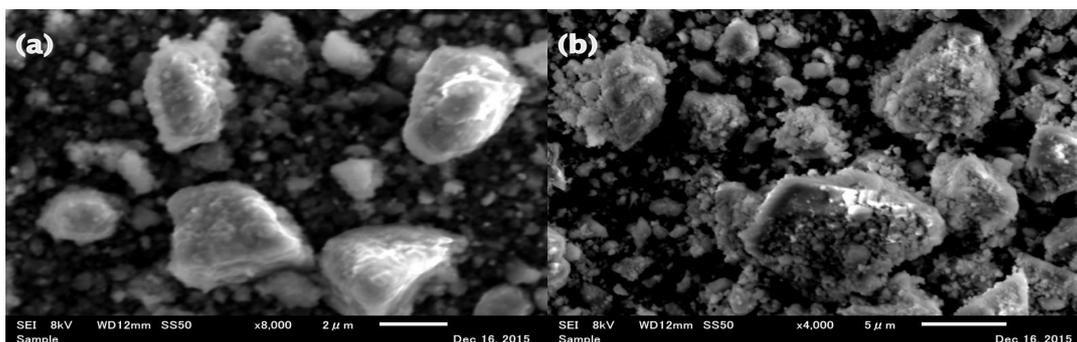


Fig. 4 Morphology of MgH<sub>2</sub> milled with (a) Nb<sub>2</sub>O<sub>5</sub> and (b) Si catalyst

In order to evaluate the decreasing particles size, scanning electron microscopy observation was conducted as shown in Fig. 3. It is clearly seen that milling of MgH<sub>2</sub> powder for 20 h decreased the particles size significantly from microcrystalline (as-received) to nanocrystalline. This resulted consequently in the formation of crystallite size as observed from the XRD patterns (Fig. 1) after 20 h of milling. Improvement on hydrogen sorption kinetics is expected with nanograins size particles. Furthermore, Fig. 4(a) and (b) show the morphology for the milled samples of MgH<sub>2</sub>+10wt%Nb<sub>2</sub>O<sub>5</sub> and MgH<sub>2</sub>+10wt%Si respectively. Both Nb<sub>2</sub>O<sub>5</sub> and Si particles were associated with Mg particles at the outer surface after the mechanical milling process. This shows that the presence of catalysts on Mg particles surface has served as a path for the diffusion of hydrogen, which directly improves the hydrogen sorption kinetics. In addition, Nb<sub>2</sub>O<sub>5</sub> and Si particles are distributed heterogeneously which can be seen in irregular shapes.

Fig. 5 shows the absorption curves of milled MgH<sub>2</sub> with and without catalysts. It can be clearly seen that the addition of a single catalyst, both Nb<sub>2</sub>O<sub>5</sub> and Si improved the absorption kinetics in comparison to MgH<sub>2</sub> milled without catalysts. The slopes of absorption curve

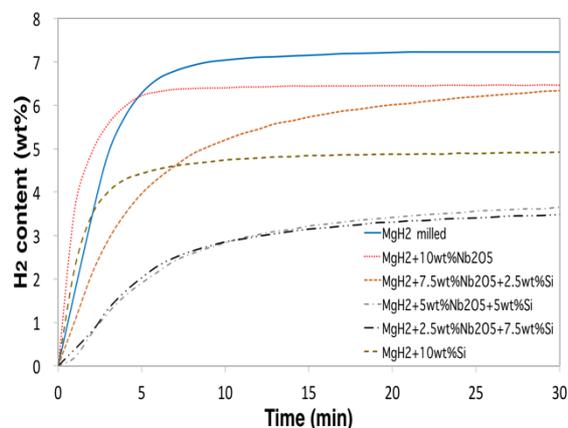


Fig. 5 Hydrogen absorption curves for milled samples at 300°C under 1 MPa hydrogen pressure.

indicate the kinetics of hydrogen absorption for all samples. Nb<sub>2</sub>O<sub>5</sub> had been identified as the most efficient catalyst for absorption in our study as it has a sharp slope, although the amount of hydrogen absorbed was less than MgH<sub>2</sub> milled without a catalyst. Almost 6 wt% of hydrogen could be absorbed only after 4 min at 300°C under 1 MPa and within 7 min, MgH<sub>2</sub>+10wt%Nb<sub>2</sub>O<sub>5</sub> absorbed 6.5 wt% of hydrogen. In fact, the theoretical capacity of MgH<sub>2</sub>+10wt%Nb<sub>2</sub>O<sub>5</sub> sample is 6.8 wt% in contrast to 7.6 wt% for MgH<sub>2</sub> without catalyst.

However, there were some differences in the

amount of hydrogen absorbed for MgH<sub>2</sub>+10wt%Si sample even though fast absorption kinetic was achieved as shown in Fig. 5. With Si addition, the absorbed Mg was approximately 4wt% of hydrogen in 3 min, while 10 min was needed to reach 4.8 wt% of hydrogen absorbed. The addition of multiple catalysts to the MgH<sub>2</sub> has no significant influence on the hydrogen absorption kinetics. Hence, the interaction between Nb<sub>2</sub>O<sub>5</sub> and Si seemed to be ambiguous as the kinetics became slower for samples with multiple additives.

#### 4. CONCLUSION

In conclusion, mechanical milling processes significantly improved the MgH<sub>2</sub> behavior by reducing the particles size which leads to the increase in specific surface area. High energy ball milling leads to the appearance of β-MgH<sub>2</sub> phase which indicates a decrease in crystallite size within the powder particles. Hydrogen desorption temperature is also shifted to a lower temperature due to the catalytic effect of Nb<sub>2</sub>O<sub>5</sub> and Si. SEM micrographs results showed that particles size decreased significantly as a result of the appearance of β-MgH<sub>2</sub> in the XRD pattern. The fastest absorption kinetics was obtained for a MgH<sub>2</sub>+10wt%Nb<sub>2</sub>O<sub>5</sub> sample which absorbs 6 wt% of hydrogen within 4 min. The analysis and discussion of the results reported above clearly demonstrate that Nb<sub>2</sub>O<sub>5</sub> has a greater catalytic effect on MgH<sub>2</sub> in comparison to Si. In our study, the interaction between Nb<sub>2</sub>O<sub>5</sub> and Si seems to be ambiguous as the kinetics become slower for samples with multiple additives. It proposes that, further study can be done on the mechanism of hydrogen sorption kinetics and destabilization of MgH<sub>2</sub> with multiple addition of Nb<sub>2</sub>O<sub>5</sub> and Si.

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