

# 수소 가압형 기계적 합금화법으로 제조한 $MgH_x-Nb_2O_5$ 산화물 복합 재료의 수소화 특성 평가

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## Evaluations of Hydrogen Properties of $MgH_x-Nb_2O_5$ Oxide Composite by Hydrogen Induced Mechanical Alloying

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**Abstract** >> Mg and Mg-based alloys are regarded as strong candidate hydrogen storage materials since their hydrogen capacity exceeds that of known metal hydrides. One of the approaches to improve kinetic is addition of metal oxide. In this paper, we tried to improve the hydrogenation properties of Mg-based hydrogen storage composites. The effect of transition metal oxides, such as  $Nb_2O_5$  on the kinetics of the Magnesium hydrogen absorption kinetics was investigated.  $MgH_x$ -5wt.%  $Nb_2O_5$  composites have been synthesized by hydrogen induced mechanical alloying. The powder fabricated was characterized by X-ray diffraction (XRD), Field Emission-Scanning Electron Microscopy (Fe-SEM), Energy Dispersive X-ray (EDX), BET and simultaneous Thermo Gravimetric Analysis / Differential Scanning Calorimetry (TG/DSC) analysis. The Absorption / desorption kinetics of  $MgH_x$ -5wt.%  $Nb_2O_5$  (type I and II) are determined at 423, 473, 523, 573 and 623 K.

**Key words** : Hydrogen storage alloy (수소저장합금), Mechanical alloying (기계적 합금화법), Hydride (수소화물), Kinetics(반응속도)

### 1. Introduction

Hydrogen energy will be used instead of coal and petroleum in the near future, but obstructing factors must first be solved, such as cost efficiency, social infrastructure and stability. In hydrogen related research hydrogen storage is an most important projects for hydrogen economical society. One of the key tech-

nologies is to develop high-performance hydrogen storage materials. Gasification or liquefaction of hydrogen storage were not more stable than hydrogen storage in metal. For hydrogen storage, metallic hydrides with a high storage capacity are preferred to the compressed or liquid hydrogen, due to high volumetric capacity, safety and convenience. However, many problems need to be resolved: weight per hydrogen capacity, high operating temperature, slow kinetics and the initial activation process<sup>1)</sup>. In particular, magnesium hydride is one of the most attractive materials

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[ 접수일 : 2012.7.31 수정일 : 2012.8.27 게재확정일 : 2012.10.26 ]

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because that is directly combined from the reaction of Mg with hydrogen and reaches a high hydrogen capacity (7.6 wt.%). Moreover, it is environmentally benign, abundant, inexpensive and easy to handle. However, for pure magnesium, its high operating temperature, high thermodynamic stability of  $MgH_2$  (-75 kJ/mol) and slow kinetics prevent it from being used for practical applications<sup>2)</sup>.

Several ways have been reported to enhance the sorption kinetics of magnesium-based hydrides including particle size reduction by high energy ball milling<sup>3)</sup> and Carbon addition<sup>4)</sup>. A successful route remains the addition of transition metals<sup>5-8)</sup>, oxides<sup>9)</sup>, halides<sup>10-11)</sup>, carbides and nitrides<sup>12)</sup>. Among the transition metals, oxides act as a good catalyst and enable  $MgH_2$ -based composites to decrease the operation temperature, improving the hydrogen absorption/desorption properties by adding a transition metal oxide, for example, Nb, V or Fe. Metal oxide materials have a catalytic effect on the research<sup>12,13)</sup>. Especially, W. Oelerich, et al<sup>13)</sup> reported that hydriding/dehydriding properties of nanocrystalline  $MgH_2$  improved through 0.05 wt.% transition metal oxide addition (CuO,  $Mn_2O$ ,  $Cr_2O_3$ ,  $Fe_3O_4$  and  $V_2O_5$ ). The kinetics of  $MgH_2$ -0.05 wt.% transition metal oxide composites was faster than  $MgH_2$  without catalysts.

However, it is not yet clear what the mechanism of catalysis for oxides is, and which oxides are most effective. One of the empirical rules claims better efficiency for oxides, in which metal atoms have multiple valence states<sup>12,13)</sup>. In this work, the transition metal oxide should have a positive effect on the hydriding/dehydriding reaction of nanocrystalline Mg. Investigations concerning the absorption properties of nanocrystalline  $MgH_x$  with and without  $Nb_2O_5$  catalyst on different temperature experiments are presented which improves to hydrogenation properties of  $MgH_x-Nb_2O_5$  composites by mechanical alloying.

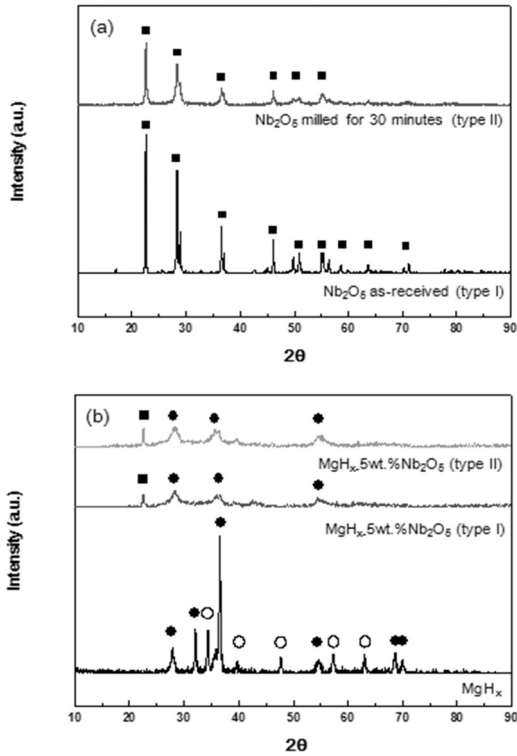
## 2. Experimental Procedure

Magnesium ingot (3 N) was fabricated to chips using a drilling machine. Hydrogen induced mechanical alloying (HIMA) was carried out in a Fritsch P5 planetary ball mill with a ball to chips weight ratio of 40:1 under 2 MPa hydrogen atmosphere and being milled for up to 48 hours. The nanocrystalline magnesium hydride powder was synthesized by mechanical alloying with 5 wt.%  $Nb_2O_5$  and then milled for up to 24 hours.  $Nb_2O_5$  (type I, 1  $\mu m$ , 3 N, Semiconductor Material Co.) were premilled to get through high energy mill that was fabricated to nano-structured  $Nb_2O_5$  (type II). Premilling was carried out with a zirconia-ball to  $Nb_2O_5$  powder ratio of 10:1 in a zirconia vessel and then milled for up to 30 minutes.  $MgH_x$  and  $MgH_x$ -5 wt.%  $Nb_2O_5$  (type I, II) composites synthesis were characterized as XRD, BET, SEM/EDX and TG/DSC. The kinetic properties of  $MgH_x$  and  $MgH_x$ -5 wt.%  $Nb_2O_5$  composites were performed at 423, 473, 523, 573 and 623 K under 3 MPa hydrogen atmosphere for an hour, respectively, using a volumetric Sievert's apparatus.

## 3. Results and Discussions

### 3.1 Analysis of $MgH_x$ and $MgH_x$ -5wt. % $Nb_2O_5$ composites

Fig. 1 shows XRD patterns of  $Nb_2O_5$  (type I and II),  $MgH_x$  and  $MgH_x$ -5wt.%  $Nb_2O_5$  (type I and II) composites. XRD patterns of as-received  $Nb_2O_5$  (type I) only compared with  $Nb_2O_5$  that was milled for 30 minutes (type II). When the XRD patterns of premilled  $Nb_2O_5$  (type II) was composed of highly sharp and broad peaks which is assumed like amorphous/nano-structured  $Nb_2O_5$ . To get amorphous/nano-structured  $Nb_2O_5$ , milling should be performed for longer than 30 minutes.

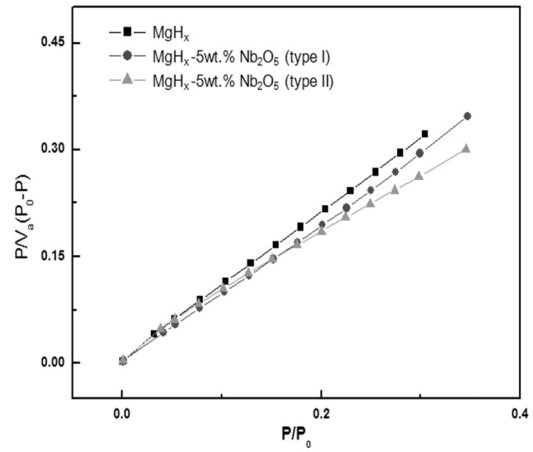


**Fig. 1** The XRD patterns of Nb<sub>2</sub>O<sub>5</sub> (a) and MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I and II) (b) composites (■; Nb<sub>2</sub>O<sub>5</sub>, ●; MgH<sub>2</sub>, ○; Mg)

XRD patterns of MgH<sub>x</sub> exhibits mainly the peaks corresponding to the MgH<sub>2</sub> phase with a small quantity of pure Mg. The results of XRD indicated that there was no apparent reaction between the Nb<sub>2</sub>O<sub>5</sub> (type I and II) powder and the MgH<sub>x</sub> during HIMA. The XRD peaks of Nb<sub>2</sub>O<sub>5</sub> added to the magnesium hydrides, MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I and II) did not show any shift in XRD peak positions. The MgH<sub>x</sub> peaks remained sharp and strong intense, due to the polycrystalline MgH<sub>2</sub>. On the contrary, XRD patterns of MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I and II) showed broad MgH<sub>2</sub> peaks, of which intensity decreased with MgH<sub>2</sub> concentration that was like-amorphous / nano-structured MgH<sub>2</sub> when 29° and 36°. Simultaneous to the Nb<sub>2</sub>O<sub>5</sub> (type I and II) addition, the MgH<sub>2</sub> diffraction peaks broadened, and their intensity decreased, indicating a significant

**Table 1** Results of BET on MgH<sub>x</sub> and MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I and II) composites

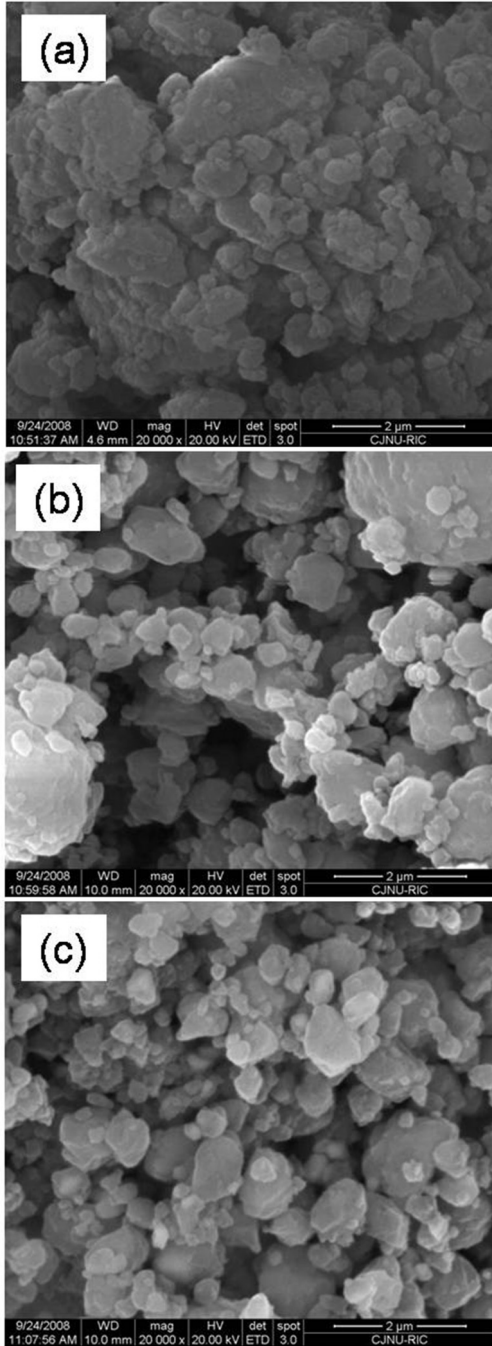
	as, BET (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
MgH <sub>x</sub>	4.2571	0.0021	1.9760
MgH <sub>x</sub> -5 wt.% Nb <sub>2</sub> O <sub>5</sub> (type I)	4.5901	0.0024	2.0655
MgH <sub>x</sub> -5 wt.% Nb <sub>2</sub> O <sub>5</sub> (type II)	5.2490	0.0027	2.0719



**Fig. 2** BET analysis of MgH<sub>x</sub> and MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I and II)

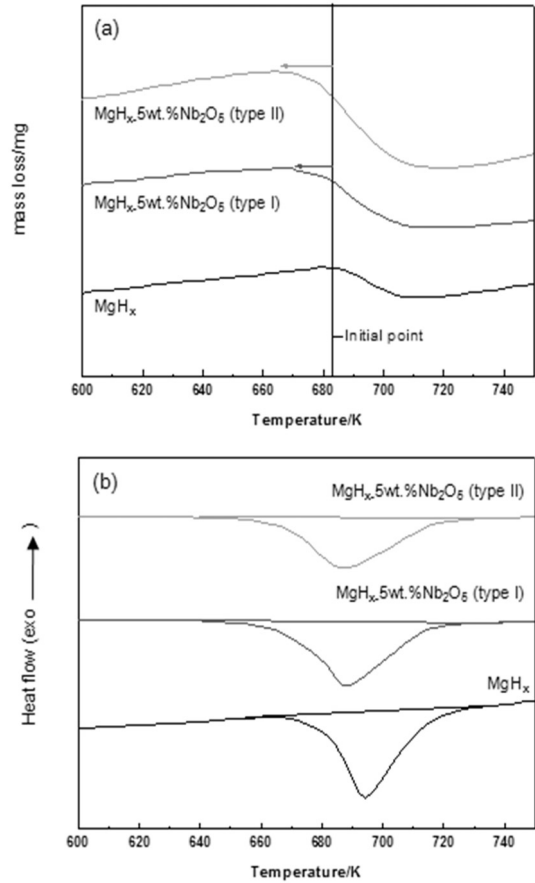
particle size reduction and modification of the micro-structure of the magnesium hydride. Results showed such evolution was dependent on the morphology and/or surface area of MgH<sub>x</sub> and MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I and II), as it was stronger for MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I) as compared to the MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type II). Indeed, the BET of MgH<sub>x</sub> (Fig. 2) increased from 4.3 to 4.6 and 5.2 m<sup>2</sup>/g for MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I) and MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type II) composites, respectively. If the MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> composite has increasing surface area, maybe it will continue to improve hydrogenation properties, because hydrogen diffusion generates at the grain boundary<sup>14</sup>.

High energy milling can also induced particle size reduction which could influence kinetics. Therefore, the powder obtained was investigated by SEM. Respec-



**Fig. 3** SEM morphologies of  $\text{MgH}_x$  (a),  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type I) (b) and  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type II) (c) composites

tive micrographs (Fig. 3) indicated that the particle size of  $\text{MgH}_2$  effectively decreased during HIMA. After



**Fig. 4** TG (a) / DSC (b) analysis of  $\text{MgH}_x$  and  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type I and II) composites

48 hours of milling, particle sizes in the range of 30 nm to 15  $\mu\text{m}$  are observed for  $\text{MgH}_x$  (Fig. 3(a) and (b)). If milled with  $\text{Nb}_2\text{O}_5$ , the average particle size appeared smaller, i.e. more nanometric particles could be imaged (c). Fig. 3 presented the distribution of  $\text{MgH}_x$  and  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type I and II) particle size as determined by the analysis of the Fe-SEM images. For  $\text{MgH}_x$ , the particle size distribution was observed 30 nm to 2  $\mu\text{m}$ .

With the  $\text{Nb}_2\text{O}_5$  addition, the distribution was 30 nm to 15  $\mu\text{m}$ . The  $\text{Nb}_2\text{O}_5$  particles, with an average initial size of 3  $\mu\text{m}$ , were also broken upon milling into particles with a large size distribution. Especially,

distribution of  $MgH_x$ , in the mass, was larger than  $MgH_x$ -5 wt.%  $Nb_2O_5$  (type I and II) composites.

The hydrogen desorption properties of composites synthesized can be deduced from TG/DSC profiles. As can be seen in Fig. 4, there was almost no difference in the thermal behavior among the three samples. The main decomposition reaction started at around 682 K on  $MgH_x$  and decreased the initial temperature. Therefore, the effects of  $Nb_2O_5$  was decreasing the operating temperature and increasing dehydrogenation quantity through a change in the initial temperature and mass loss quantity. A mass loss quantity of  $MgH_x$  and  $MgH_x$ -5 wt.%  $Nb_2O_5$  (type I and II) showed 0.1, 0.24 and 0.38 mg, respectively. The reaction enthalpy,  $\Delta H$ , was decreasing which easily happens in the endothermic reaction<sup>15)</sup>. Respectively, the  $\Delta H$  of  $MgH_x$  and  $MgH_x$ -5 wt.%  $Nb_2O_5$  (type I and II) were calculated -1234, -1196 and -1056 J/g. The mass loss quantity was increasing and  $\Delta H$  was decreasing during HIMA.

### 3.2 Hydrogenation/dehydrogenation of $MgH_x$ and $MgH_x$ -5 wt. % $Nb_2O_5$ (type I and II) composites

Fig. 5 (a) shows absorption curves for a sample of milled  $MgH_x$  without  $Nb_2O_5$  at 423, 473, 523, 573 and 623 K under 3 MPa hydrogen atmosphere. As can be clearly seen, the absorption rate was faster when the temperature was increased.

The hydrogen capacities of  $MgH_x$  was measured 0.37 wt.% at 423 K, 1.69 wt.% at 473 K, 5.08 wt.% at 523 K, 5.22 wt.% at 573 K and 5.06 wt.% at 623 K. The absorption profile of  $MgH_x$  at 423 and 473 K, were observed non-activated reaction slope. For sufficient absorption to occur, more than 1 hour is needed with low operating temperature. The desorption of  $MgH_x$  was only presented at 623 K and kinetics

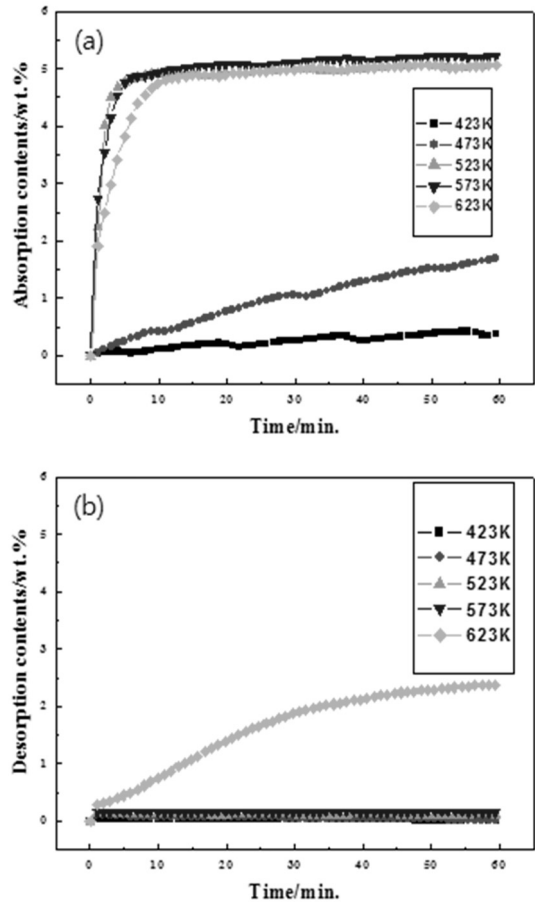
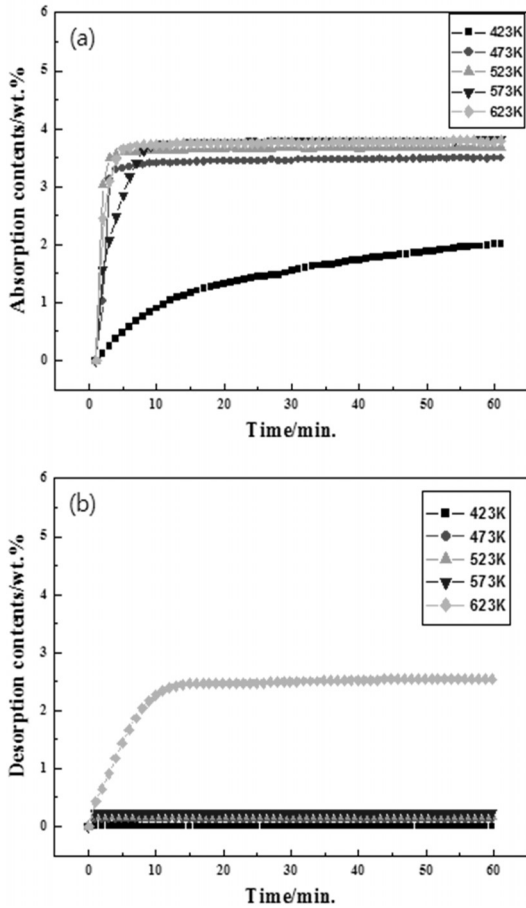


Fig. 5 Absorption profile of  $MgH_x$  under 3 MPa (a) and desorption profile of  $MgH_x$  under vacuum (b) composites

was very slow, see Fig. 5 (b). The desorption was not clear reaction which needs more time and a high operating temperature.

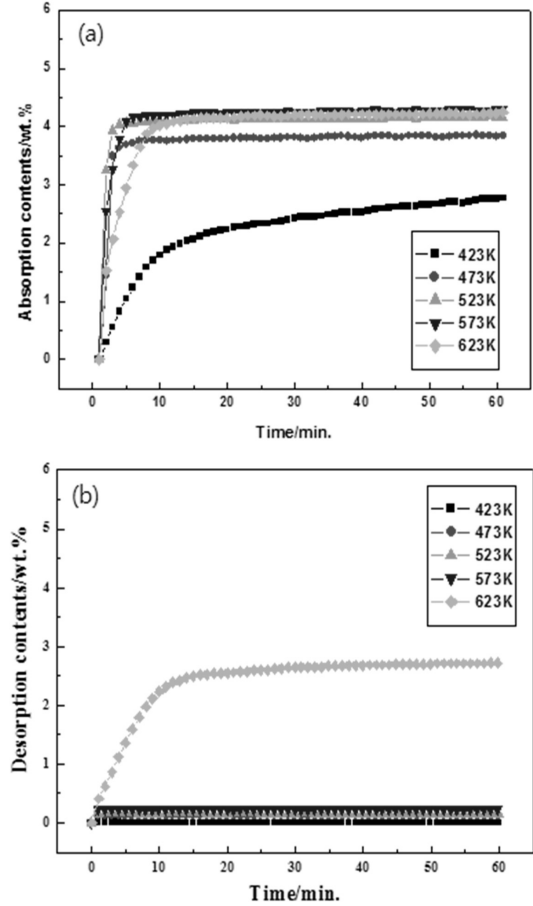
The absorption rate between the initial time and 4 minutes of the set point reaches 0.00029 wt.%/s at 423 K, 0.00088 wt.%/s at 473 K, 0.01954 wt.%/s at 523 K, 0.01891 wt.%/s at 573 K and 0.01425 wt.%/s. The fastest absorption kinetics showed at 473K. However, the absorption properties of magnesium hydride had very slow kinetics at low operating temperatures.

The hydrogen capacities of  $MgH_x$ -5 wt.%  $Nb_2O_5$  (type I) composites was measured 2.01 wt.% at 423 K, 3.49 wt.% at 473 K, 3.81 wt.% at 523 K, 3.79



**Fig. 6** Absorption profile of  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type I) under 3 MPa (a) and desorption profile of  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type I) under vacuum (b) composites

wt.% at 573 K and 3.79 wt.% at 623 K (see Fig. 6 (a)). The absorption rate was clearly faster with the addition of  $\text{Nb}_2\text{O}_5$ , especially at 473 K. However, hydrogen capacities had lower  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type I) composites than  $\text{MgH}_x$ . The absorption rate between the initial time and 4 minutes of the set point reached 0.00196 wt.%/s at 423 K, 0.01383 wt.%/s at 473 K, 0.01496 wt.%/s at 523 K, 0.01188 wt.%/s at 573 K and 0.1521 wt.%/s at 623 K. The best temperature was 523 K in hydrogen capacity and the best hydrogen storage rate was 623 K in kinetics. Fig. 6 (b) shows the desorption of  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$



**Fig. 7** Absorption profile of  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type II) under 3 MPa (a) and desorption profile of  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type II) under vacuum (b) composites.

(type I) composite, that only showed the desorption reaction at 623 K. The desorption quantity was 2.5 wt.% when 623 K, but that was a very small quantity to compare with the hydrogen capacity.

Therefore, the high surface area of  $\text{Nb}_2\text{O}_5$  should have a positive effect on the hydrogen diffusion which was improve to hydrogenation/dehydrogenation properties<sup>16)</sup>.

Fig. 7 (a) shows the absorption profile of  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type II) composites. The absorption rate of  $\text{MgH}_x\text{-5 wt.}\% \text{Nb}_2\text{O}_5$  (type II) composites was measured 0.00433 wt.%/s at 423 K, 0.01541 wt.%/s

at 473 K, 0.01691 wt.%/s at 523 K, 0.01704 wt.%/s at 573 K and 0.0123 wt.%/s, and the hydrogen capacities of MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type II) composites were 2.77 wt.% at 423 K, 3.84 wt.% at 473 K, 4.17 wt.% at 523 K, 4.30 wt.% at 573 K and 4.25 wt.% at 623 K when between the initial time and 4 minutes and between the initial time and 5 minutes, respectively.

The hydrogen capacities of MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type II) composites was more than MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I) composites and improving kinetics of MgH<sub>x</sub>. Fig. 7 (b) shows the desorption profile of MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type II) composites. The hydrogen desorption quantity was 2.72 wt.% which was more than MgH<sub>x</sub> and MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I) composites at 623 K, but more time is needed and temperature should be higher than 623 K.

#### 4. Conclusion

In this report was preformed evaluation of hydrogenation properties on MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I and II) composites in the temperature ranges of 423, 473, 523, 573 and 623 K under 3 MPa hydrogen atmosphere. The kinetics of MgH<sub>x</sub> was found to be very slow. Hydrogenation/dehydrogenation kinetics of MgH<sub>x</sub> was improved by addition of Nb<sub>2</sub>O<sub>5</sub> (type I and II). However, MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I and II) composites was decreased hydrogen capacity more than MgH<sub>x</sub>. Especially, hydrogenation/dehydrogenation kinetics of MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type II) composite was improved more than MgH<sub>x</sub>-5 wt.% Nb<sub>2</sub>O<sub>5</sub> (type I) composite due to increasing surface area of Nb<sub>2</sub>O<sub>5</sub> (type II).

Therefore, Hydrogenation properties was improved to addition of Nb<sub>2</sub>O<sub>5</sub> and the high surface area of Nb<sub>2</sub>O<sub>5</sub> (type II) was increased the hydrogen storage rate without decreasing hydrogen capacities. However, the mechanism of catalysis is not yet clear. Further

experimentation is necessary to determine the catalyst mechanism.

#### Acknowledgement

The research was supported by a grant from the Academic Research Program of Korea National University of Transportation in 2012.

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