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기계적 합금화법에 의한 Mg_2Ni-(5, 10mass%)NbH_x 복합재료의 수소화 특성

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Hydrogenation Properties of Mg_2Ni-(5, 10mass)NbH_x Composites by Reactive Mechanical Alloying

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ABSTRACT

Mg 및 Mg합금은 수소 저장량이 7.6wt.%로 비교적 높고 자원도 풍부하여 값이 싼 장점을 가지고 있으나 산화반응성이 높고 활성화 에너지가 크기 때문에 반응온도가 높고 반응시간이 긴 단점을 가지고 있다. 이러한 단점을 극복하기 위해 일반적으로 Mg 및 Mg합금의 표면 개질화, 금속간 화합물 형성, 전이금속 첨가에 대한 연구가 활발히 진행되고 있다. 본 연구에서는 전이금속인 Nb를 촉매제로 사용하여 수소화 특성을 개선하고자 기계적 합금화법(MA;Mechanical Alloying)을 실시하여 복합재료를 합성한 후 수소화 반응을 평가하였다. XRD, SEM, TEM, PSA, TG/DSC 분석을 수행하였으며 Sievert's 형 PCT를 이용하여 온도 및 압력 변화에 따른 특성평가를 하였다. 전이금속인 Nb의 첨가로 수소화 반응개시온도가 낮아지고 수소 저장량이 향상되는 거동을 보였다. 특히, 5mass%Nb가 10mass%Nb 보다 수소 저장량 및 반응속도가 좋은 결과를 보였다.

KEY WORDS : Hydrogen storage materials(수소저장재료), Hydrogenation properties(수소화 특성), Reactive mechanical alloying(기계적 합금화법), Kinetics(반응속도), Mg_2Ni-NbH_x

1. Introduction

Magnesium and Magnesium-based alloys are considered to be promising storage media because

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of their hydrogen storage capacity (7.6wt.% for pure Mg), low density, low cost and high availability[1]. The intermetallic compound Mg_2Ni can absorb up to 3.6wt.% H_2 with the formation Mg_2NiH_4, but its reaction kinetics are very poor and the hydride is too stable for most practical applications[2].

The improvement of hydrogen absorption kinetics has been achieved by various treatments[3-6], especially by intensive milling of Mg-based alloys with some transition metal additives. Addition of transition metals (Ti, Nb, Fe, Co, V) has been used to facilitate the hydriding and dehydriding processes. The transition metals on the magnesium surface catalyze the dissociate chemisorptions of hydrogen[7-9]. In the present paper, we investigated the hydriding/dehydriding kinetics of a Mg_2Ni-(5,10mass%)NbH_x composites prepared by reactive mechanical alloying. The effect of added Niobium has been shown to increase absorption kinetics that increase with temperature.

2. Experimental

Mg_2Ni was prepared by reactive mechanical alloying under a hydrogen atmosphere for 72hrs. Mg (3N, Ingot) chips were formed by drilling, and a Ni (3N, powder) stoichiometric ratio of 45:55 charged was achieved in a STS304 Jar of 450cc. The ball to chip (BCR) weight ratio was 66:1. Then, Mg_2NiH_x synthesized with 5,10mass% Nb (3N, powder) was milled for 24 hrs using the Planetary ball mill (FRITSCH Co., Pulverisette-5). The prepared samples were handled in a glove box filled with purified argon to avoid the influence of oxidation and moisture. The particles synthesized were characterized by X-raydiffraction with CuKα radiation (XRD, RIGAKU Co., RINT2000). The morphology and composition of the particles was observed using scanning electron microscopy (SEM, HITACHI Co., S-2400) with energy dispersive spectroscopy (EDS). The micro structures of particles were observed through transmission electron microscopy (TEM, HITACHI Co., H-9000-NA). The size distribution of particles synthesized was observed by laser particle size analysis (HORIBA, LA-300). The dehydrogenation behaviors of reactive mechanical alloyed Mg_2NiH_x were measured by thermogravimetric analysis and differential scanning calorimetric (TG/DSC, NETZSCH Co., STA 409PC - Luxx). This was carried out in a pure argon atmosphere heated up to 773K at 10K/min. The hydrogen storage properties were evaluated using an automatic sievert's type automatic Pressure-Composition-Temperature (PCT) apparatus at 423, 473, 523, and 573K.

3. Results and discussion

Fig. 1 shows XRD patterns of the Mg_2NiH_x ball-milled for 72hrs under hydrogen atmosphere and Mg_2Ni-(5,10mass%) NbHx composites ball milled for 24hrs under hydrogen. There are three main peaks that can be seen by using JCPDS:Mg_2NiH_4, $NbH_{0.9}$ and Nb. The $NbH_{0.9}$ was made form Niobium hydrides with H contents during hydrogen induced

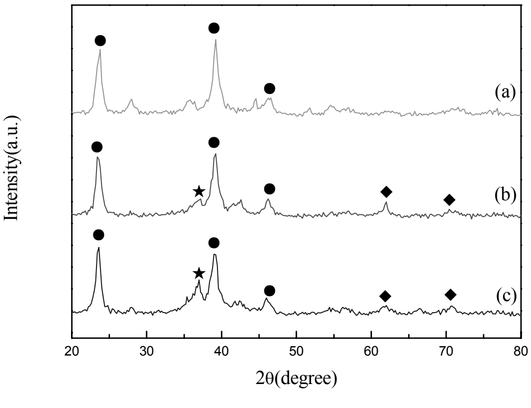

Fig. 1 XRD patterns of Mg_2NiHx(a), Mg_2Ni-5mass%NbH_x(b) and Mg_2Ni-10mass%NbH_x(c) composites. (●:Mg_2NiH_4,★:$NbH_{0.9}$,◆:Nb)

mechanical alloying.

The results for calculating the $NbH_{0.9}$ area of Mg_2Ni-10mass%NbH_x composites are wider than Mg_2Ni-5mass%NbH_x composites. It is estimated that Mg_2Ni-10mass% NbH_x composites are rich in Niobium contents. In addition, the diffraction patterns were broadened because of particle size reduction and strain accumulation during milling.

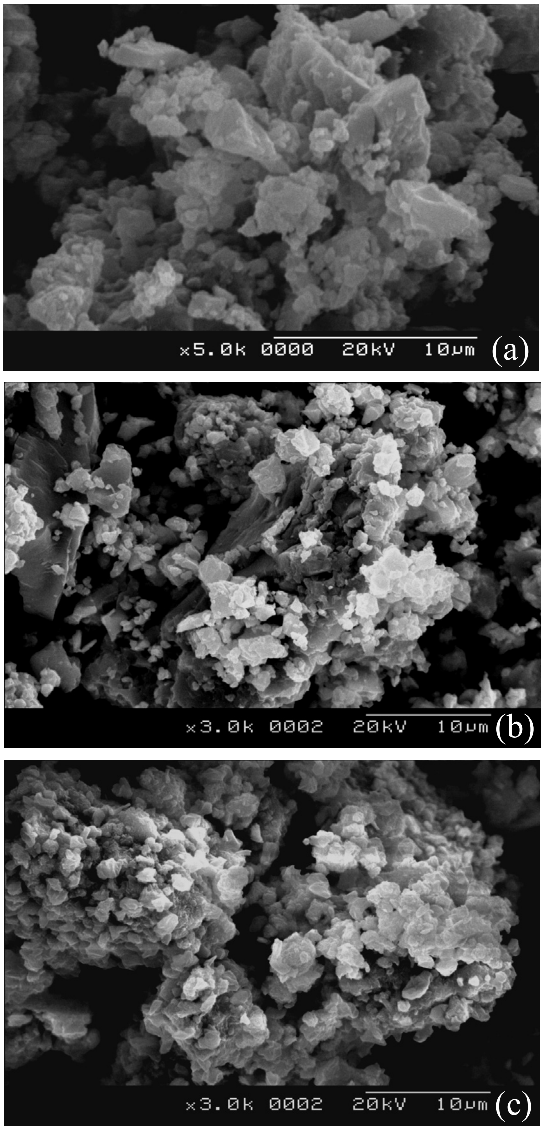

Fig. 2 SEM image of Mg_2NiH_x(a), Mg_2Ni-5mass%NbH_x(b), and Mg_2Ni-10mass%NbH_x(c) composites.

Fig. 2 shows the microstructure on a Mg_2Ni-(5,10mass%) NbH_x composite after mechanical alloyed by SEM. Some agglomerates of fine particles were also formed in Mg_2Ni+Nb.

The Mg matrix revealed mainly that the particles of 10㎛ were dispersed on the surface of relatively large particle or agglomerates of other fine particles. Mg matrix particles are usually agglomerates of smaller Mg particles and catalyst particles. Niobium powder particles after milling are characterized by small size and inhomogeneous distribution within

Table 1 Results of EDX on Mg_2NiH_x(a), Mg_2Ni-5mass%NbH_x(b), and Mg_2Ni-10mass%NbH_x(c) composites

	element	weight%	Atomic%
a	Mg Kα	69.2	72.1
	Ni Kα	31.8	27.9
b	Mg Kα	60.2	62.6
	Ni Kα	34.8	35.3
	Nb Kα	6.0	3.1
c	Mg	65.1	67.4
	Ni Kα	26.8	27.6
	Nb Kα	8.1	6.0

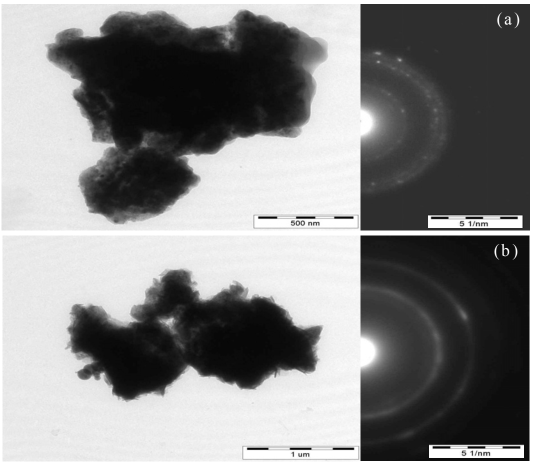

Fig. 3 TEM results of Mg_2Ni-5mass%NbH_x(a), and Mg_2Ni-10mass%NbH_x(b) composites.

the Mg-matrix particles. Overall, the particles agglomerated were discovered to be a size of approximately 1~20㎛. In addition, from the results of energy dispersive spectroscopy analysis, the composites were confirmed to harmonize with raw materials.

The microstructure of the composite was examined using TEM analysis, as shown in Fig. 3. The bright field image of Mg_2Ni-5,10mass%NbH_x composites show that the particle size is about 1 ㎛. Among the diffraction ring patterns, the partially spotty ring patterns were indicated by the Möirfringe effect.

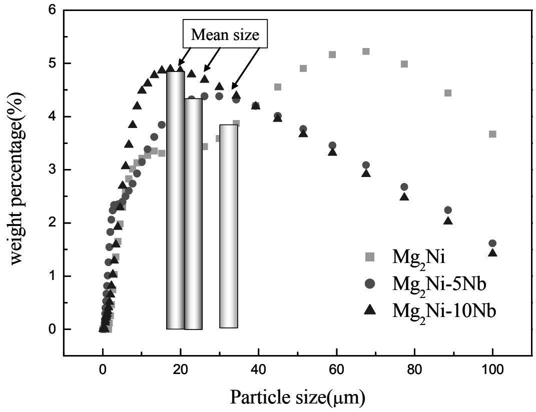

Fig. 4 Particle size distributions on Mg_2NiH_x and Mg_2Ni-(5,10 mass%) NbH_x composites.

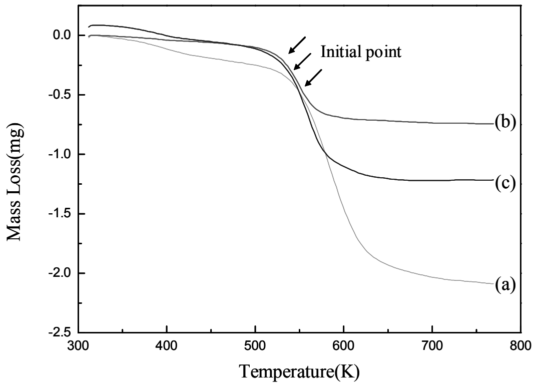

Fig. 5 The TGA curves of Mg_2NiH_x(a), Mg_2Ni-5mass%NbH_x (b) and Mg_2Ni-10mass% NbH_x(c) composites.

Fig. 4 shows the evolution of the particle size of Mg_2NiH_x and Mg_2Ni-5,10mass% NbH_x composites. A mean size of Mg_2NiH_x agglomerated particle size close to 35.02㎛. However, the mean size of Mg_2Ni-5,10mass% NbH_x composites was 23.42㎛, 23.63㎛ respectively. In addition, the median size Mg_2Ni-5,10mass% NbH_x composites was15.53 ㎛, 16.09㎛ respectively. We found that Mg_2Ni with Niobium powder were smaller than the synthesized Mg_2NiH_x particles size. Therefore, it is believed that addition to Niobium may be pulverized more effectively during reactive mechanical alloying.

TG curves of Mg_2Ni-(5,10mass%) NbH_x composites are shown in Fig. 5. In this case, a decrease in mass of each composite due to adsorptions of absorbed hydrogen started at about 523K, indicating that the hydrides of these composites have similar thermodynamic stabilities. Furthermore, the

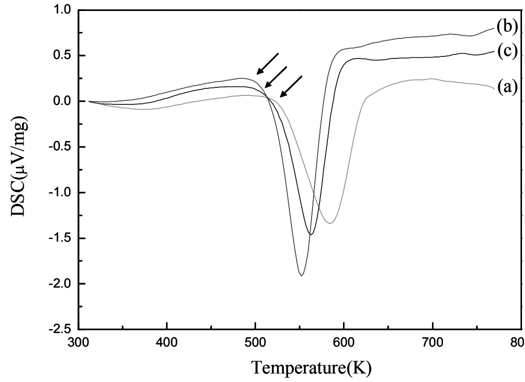

Fig. 6 The DSC curves of Mg_2NiH_x(a), Mg_2Ni-5mass%NbH_x(b) and Mg_2Ni-10mass% NbH_x(c) composites.

Table 2 Summary of the Mg_2NiH_x and Mg_2Ni-(5, 10mass%) NbH_x composites DSC data

	Onset point (K)	ΔH (Jg^{-1})
Mg_2Ni	533.9	2010
Mg_2Ni-5Nb	525.8	2205
Mg_2Ni-10Nb	535.2	1878

Mg_2Ni-10mass% NbH_x composites desorbed hydrogen of a larger amount than the Mg_2Ni-5mass% NbH_x composites. For Mg_2Ni-(5,10mass%) NbH_x composites, the mass loss reached 0.75 and 1.25mg, respectively.

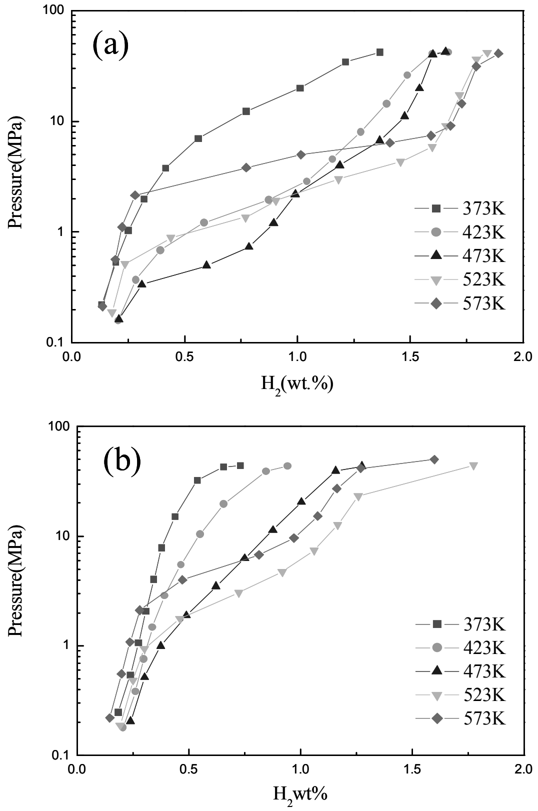

Fig. 7 Hydriding profiles of Mg_2Ni-5mass%NbH_x(a), and Mg_2Ni-10mass%NbH_x(b) composites.

Table 3 Hydrogen Absorption Capacity in 3600sec of the Mg_2NiH_x and Mg_2Ni-(5,10mass%)NbH_x composites measured at different temperatures.

Temp. (K)	Hydrogen Storage Capacity (wt.%)		
	Mg_2Ni	Mg_2Ni-5Nb	Mg_2Ni-10Nb
423K	0.25	2.0	1.8
473K	1.0	2.5	2.18
523K	1.6	2.65	2.22
573K	2.2	3.0	2.28

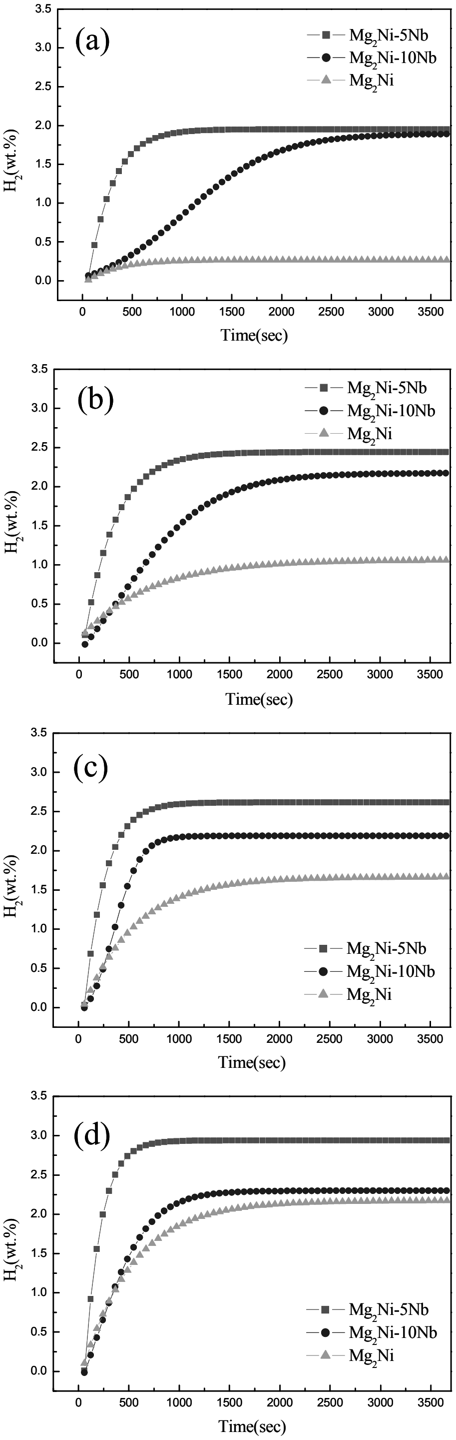

Fig. 8 Hydrogen Absorption kinetics behaviors of Mg_2NiH_x and Mg_2Ni-(5,10mass%)NbH_x composites at 423K(a), 473K(b), 523K(c), and 573K(d).

Fig. 6 shows the DSC curves obtained with the heating rate of 10K/min. The endothermic reaction of Mg_2NiH_x and Mg_2Ni-5,10mass% NbH_x composites is seen to start around 533.9, 525.8, 535.2K, respectively. Table 3 shows the parameters determined from the DSC curves. The enthalpy change of desorption. The $\triangle H$ was calculated from the endothermic peak area by the DSC.

Fig. 7 shows the hydriding profile of Mg_2NiH_x and Mg_2Ni-5,10mass% NbH_x composites by using pressure-composition- temperature (PCT) with activation. In PCT profiles, total hydriding reactions lope was difficult to observe in the phase ($\alpha+\beta$) coexistence region, namely for plateau pressure. The plateau pressure appears above 523K. With increasing temperature, maximum hydrogen storage was increasing.

The kinetics curves of hydrogen absorption by Mg_2NiH_x and Mg_2Ni-5,10mass% NbH_x composites at different temperatures and a pressure of 1.0MPa are shown in Fig. 8.

The hydrogenation absorption kinetic was evaluated using the automatic volumetric method. The hydrogen absorption kinetics were compared for 72hrs for the ball-milled Mg_2NiH_x curves. All the composites exhibited fast kinetics and reached maximum absorption capacity within 3600sec. From these curves, it can be seen that Mg_2NiH_x and Mg_2Ni-5,10mass% NbH_x composites have the same shape, suggesting that they have the same hydrogenation rate-limiting steps. The hydrogen absorption capacity is summarized in Table 3.

4. Conclusions

Hydrogen absorption properties of Mg_2Ni-5,10 mass% NbH_x composites are prepared by reactive mechanical alloying. Mg_2Ni-5,10mass% NbH_x composites have been compared for 72hrs ball-milled Mg_2NiH_x profiles. The effect of catalytic elements additives on the hydrogen absorption properties was studied.

1) The composites revealed $NbH_{0.9}$ and Nb peaks by XRD using JCPDS. The diffraction patterns were broadened because of particle size reduction and strain accumulation during milling.
2) Niobium particles after milling are characterized by small size and inhomogeneous distribution within the Mg-matrix particles. Overall, the particles agglomerated were discovered to be a size of approximately 1～20㎛. The bright field image of Mg_2Ni-5,10mass% NbH_x composites showed that the particle size is about 1㎛. Among the diffraction ring patterns, the partially spotty ring patterns were indicated by the Möirfringe effect.
3) In the TG/DSC results, absorbed hydrogen started at about 523K and the endothermic reaction was started around 530K. For Mg_2Ni-(5,10mass%) NbH_x composites, the mass loss reached 0.75 and 1.25mg, respectively. This may be the reason for mass loss gap because $NbH_{0.9}$ contents in XRD patterns of Mg_2Ni-10mass% NbH_x composites are much higher than Mg_2Ni-5mass% NbH_x composites.
4) The absorption capacity of Mg_2Ni-5mass% NbH_x composites was found to be about 3.0wt.% at 573K under a 1MPa hydrogen atmosphere. The composite with Niobium additives showed much more rapid absorption kinetics than Mg_2NiH_x synthesized. This depends on the Niobium additives, not just on the hydrogen absorption process but also particles size reduction. Therefore, Mg_2Ni-5mass%NbH_x composites are believed to be excellent materials for hydrogenation properties.

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