

수소 분위기에서 밀링에 의해 제조한 마그네슘-니켈 합금의 수소화물 형성 및 분해 속도

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Hydriding and Dehydriding Rates of Magnesium-Nickel Alloy Fabricated by Milling under Hydrogen

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ABSTRACT

A 76.5wt%Mg - 23.5wt%Ni (Mg-23.5Ni) sample was prepared by reactive mechanical grinding (RMG) and its hydriding and dehydriding properties were then investigated. Activation of the Mg-23.5Ni sample was completed only after two hydriding (under 12 bar H₂) - dehydriding (under 1.0 bar H₂) cycles at 593K. The reactive mechanical grinding of Mg with Ni is considered to facilitate nucleation and shorten diffusion distances of hydrogen atoms. After hydriding - dehydriding cycling, the Mg-23.5Ni sample contained Mg₂Ni phase.

KEY WORDS : H₂-storage properties of Mg(Mg의 수소 저장 성질), Addition of Ni(Ni의 첨가), Reactive mechanical grinding(반응성 기계적 분쇄), Mg₂Ni formation(Mg₂Ni 형성), Mg(OH)₂ formation (Mg(OH)₂ 형성)

Nomenclature

Mg-23.5Ni : 76.5wt%Mg - 23.5wt%Ni

H_a : weight percentage of absorbed hydrogen

H_d : weight percentage of desorbed hydrogen

n : number of cycles

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1. Introduction

Efficient hydrogen storage technology is greatly required in the forthcoming hydrogen economy, in which energy is stored and transported using hydrogen as an energy carrier for mobile applications (automobiles, aircraft, laptops, etc.). Most of the research on this topic has focused on storing hy-

drogen safely in light weight, compact and high capacity systems. There are six storage methods currently being investigated: storing hydrogen as a gas, liquid hydrogen storage, the physisorption of hydrogen, and storing it in the form of metal hydrides, complex hydrides, and via chemical reactions.

Magnesium has many advantages for a hydrogen storage material such as large hydrogen storage capacity (7.6 wt%), low cost and abundance in the earth's crust. In spite of these advantages, its hydriding and dehydriding rates are very low. A lot of work to ameliorate the reaction kinetics of magnesium with hydrogen has been done by alloying certain metals with magnesium¹⁻⁹, mixing metal additives with magnesium¹⁰, plating nickel on the surface of magnesium¹¹, or synthesizing MgH_2 by hydriding chemical vapor deposition¹².

Song et al.¹³⁻¹⁶ increased the hydriding and dehydriding rates of Mg by mechanical alloying of Mg with Ni under Ar atmosphere. Bobet et al.¹⁷ reported that mechanical alloying in H_2 (reactive mechanical grinding, RMG) for a short time (2 h) is an effective way to improve the hydrogen-storage properties of both magnesium and Mg + 10 wt% Co, Ni or Fe mixtures.

Mechanically alloyed 75wt%Mg-25wt%Ni mixture showed high hydriding and dehydriding rates, and large hydrogen storage capacity^{15,16}. Yim et al.¹⁸ studied the hydriding properties of Mg - x wt% Ni (x=13.5, 23.5 and 33.5) prepared by three different methods: gravity cast, melt spinning, and crystallization heat treatment after melt spinning. The melt spinning process, which is a rapid solidification process, was used for the alloy preparation because a homogeneous mixing of constituent elements was expected in the liquid state of the melt before the spinning process. Among these nine samples, Mg-23.5wt%Ni heat-treated after melt spinning had the highest hydrogen-storage capacity and

hydriding rate.

However, this process for sample preparation (heat treatment after melt spinning) is very complicated and time-consuming. Therefore we chose a simpler process, mechanical grinding in H_2 (reactive mechanical grinding), to prepare a mixture with a composition 76.5wt%Mg-23.5wt%Ni in this work.

In this work, an Mg-23.5Ni sample was prepared by reactive mechanical grinding and its hydriding and dehydriding properties were then measured, and X-ray diffraction (XRD) analysis and observation of microstructure by scanning electron microscopy (SEM) were performed.

2. Experimental details

Pure Mg powder (particle size 297~100 μm , purity 99%, Fluka) and Ni (average particle size ~5 μm , purity 99.9%, Cerac) were used as starting materials.

Reactive mechanical grinding was done in a planetary ball mill (Planetary Mono Mill; Pulverisette 6, Fritsch). A mixture with the desired composition (total weight = 8 g) was mixed in a stainless steel container (with 105 hardened steel balls, total weight = 360 g) sealed hermetically. The sample to ball weight ratio was 1/45. All sample handling was performed in a glove box under Ar in order to prevent oxidation. The disc revolution speed was 250 rpm. The mill container was then filled with high purity hydrogen gas (≈ 12 bar). The reactive mechanical grinding was performed for 4 h (milling 2 h + refilling with H_2 + milling 2 h).

The absorbed or desorbed hydrogen quantity was measured as a function of time by a volumetric method, using Sivert's type hydriding and dehydriding apparatus described previously¹⁹. XRD analysis was carried out for the as-milled powders and for the samples after hydriding-dehydriding cycling. The micro structures were observed by SEM.

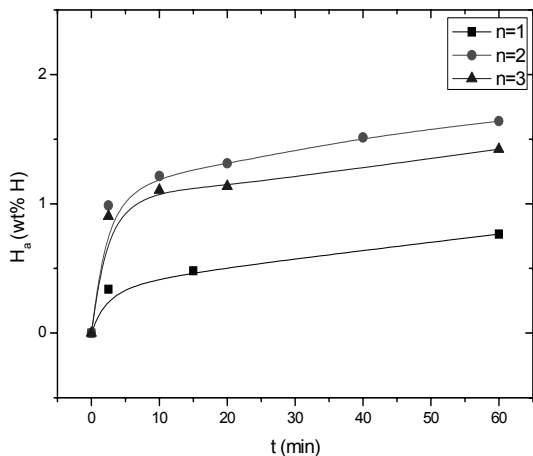


Fig. 1 Variation of the H_a versus t curve with the number of cycles for as-milled Mg-23.5Ni at 593K under 12 bar H_2

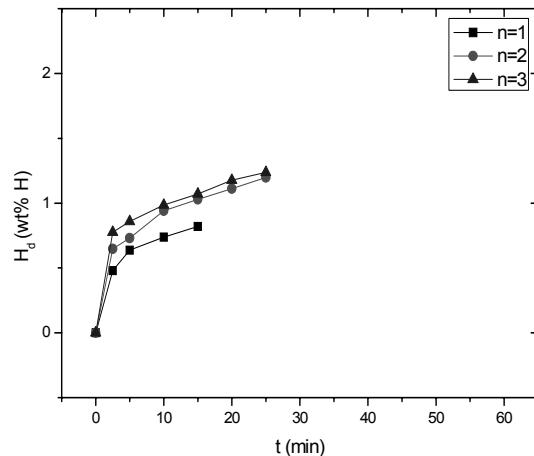


Fig. 2 Variation of the H_d versus t curve with the number of cycles for as-milled Mg-23.5Ni at 593K under 1.0 bar H_2

3. Results and discussion

Fig. 1 shows the variation of weight percentage of absorbed hydrogen H_a versus t curve with the number of cycles n for as-milled Mg-23.5Ni at 593K under 12 bar H_2 . The percentage of absorbed hydrogen H_a is expressed with respect to the sample weight. For the measurement of the curve for $n=1$, the samples were dehydrided for 2 h in vacuum at 623K. Before obtaining the curves after $n=1$, measurements of dehydriding curves were performed, and then the samples were dehydrided for 2 h in vacuum at 623K. The expansion and contraction of the hydride-forming materials with the hydriding and dehydriding reactions is considered to make defects and cracks which bring about the fragmentation of the particles, leading to the increase in the hydriding rate from $n=1$ to $n=2$. However, as the number of cycles increases from $n=2$ to $n=3$, absorbed hydrogen quantity after about 5 min decreases. The compaction and the sintering of the particles, due to the hydriding-dehydriding cycling at relatively high temperature (593K), are considered to decrease absorbed hydrogen quantity

after about 5 min. These H_a versus t curves show that the activation is completed after $n=2$. This sample absorbs 0.93 wt% for 5 min, 1.11 wt% for 10 min, and 1.42 wt% for 60 min at $n=3$.

The variation of the H_d versus t curve with the number of cycles for as-milled Mg-23.5Ni at 593K under 1.0 bar H_2 is shown in Fig. 2. The percentage of desorbed hydrogen H_d is also expressed with respect to the sample weight.

Before obtaining these curves, the sample was hydrided for 1h under 12 bar H_2 at 593K. As the number of cycles increases, the dehydriding rate increases. This sample desorbs 0.86 wt% for 5 min, 0.98 wt% for 10 min, and 1.18 wt% for 20 min at $n=3$.

Fig. 3 presents the H_a versus t curves under 12bar H_2 for activated Mg-23.5Ni at 573K and 593K, and for activated pure Mg at 593K. The hydriding rate of the activated Mg-23.5Ni at 593K is higher than that at 573K in the beginning up to 20 min, but the hydriding rate at 593K is lower than that at 573K after 20 min.

This is considered due to the decrease in the

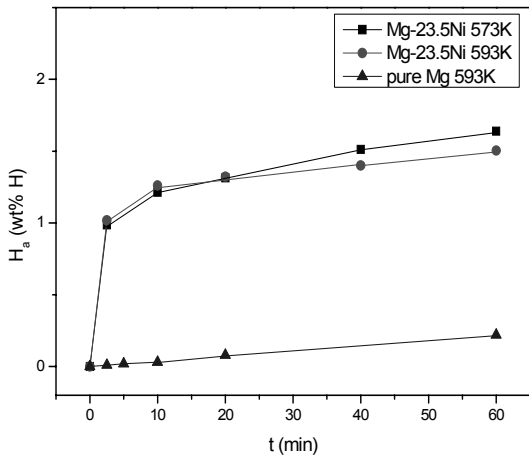


Fig. 3 H_a versus t curves under 12 bar H₂ for activated Mg-23.5Ni at 573K and 593K, and for activated pure Mg at 593K

driving force for hydriding reaction, which is related to the difference between the equilibrium plateau pressure and the hydrogen pressure (12 bar H₂), with the increase in the temperature. The activated pure Mg shows very low hydriding rate (H_a = 0.22 wt%H for 60 min).

The H_d versus t curves under 1.0 bar H₂ for activated Mg-23.5Ni at 573K and 593K, and for activated pure Mg at 593K

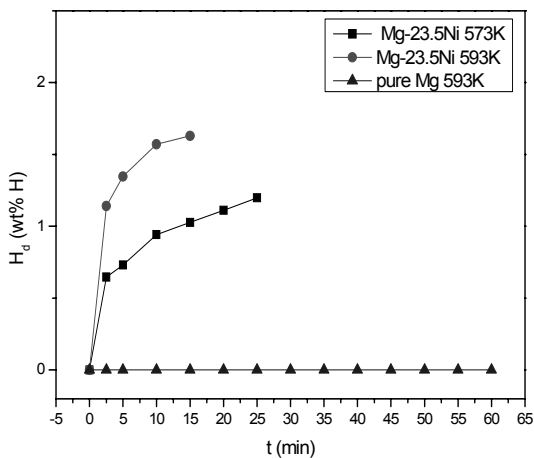


Fig. 4 H_d versus t curves under 1.0 bar H₂ for activated Mg-23.5Ni at 573K and 593K, and for activated pure Mg at 593K

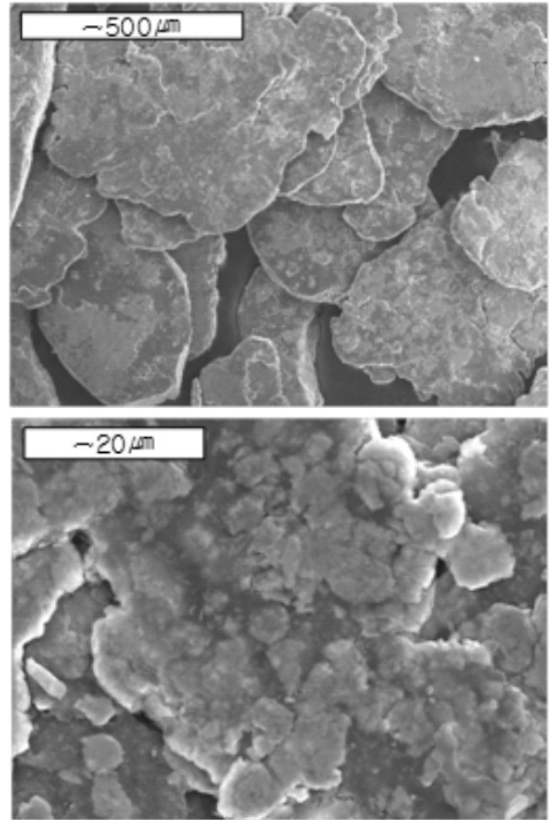


Fig. 5 Microstructure of Mg-23.5Ni after reactive mechanical grinding

activated pure Mg at 593K are shown in Fig. 4. As the temperature increases, the dehydriding rate of the activated Mg-23.5Ni increases. The activated pure Mg shows zero dehydriding rate.

Fig. 5 shows the microstructure of Mg-23.5Ni after reactive mechanical grinding. The particles are quite large and in a form of round thin plate. Small particles are agglomerated to form large particles.

The microstructure of Mg-23.5Ni after hydriding-dehydriding cycling (n=3) is presented in Fig. 6. The sample has a larger number of small particles and finer particles, and relatively large particles which is formed by the agglomeration of small or

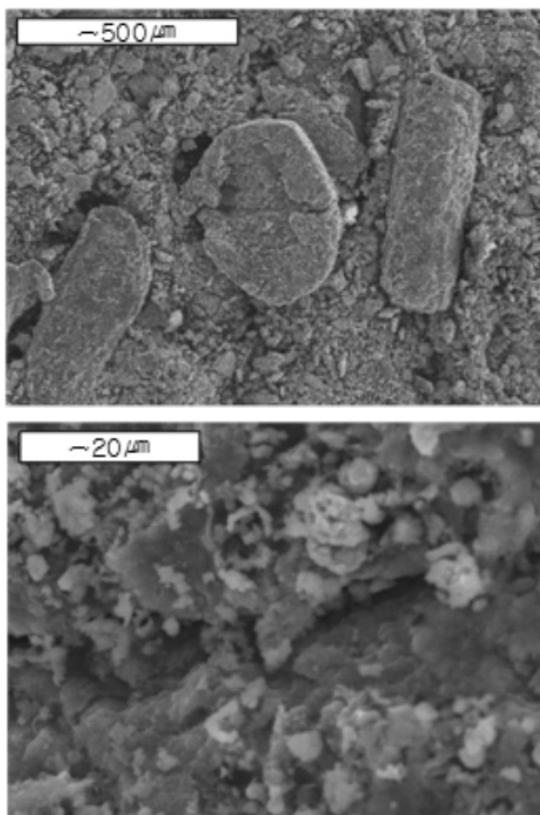


Fig. 6 Microstructure of Mg-23.5Ni after hydriding-dehydriding cycling (n=3)

fine particles. The particles are much finer than those after RMG.

The expansion and contraction of the hydride-forming materials (Mg and Mg₂Ni) with the hydriding and dehydriding reactions is considered to make defects and cracks which lead to the fragmentation of the particles into fine particles.

Fig. 7 shows the XRD pattern of Mg-23.5Ni after reactive mechanical grinding. The sample contains Mg and Ni. The XRD pattern of Mg-23.5Ni after hydriding-dehydriding cycling contained Mg and Mg₂Ni phases. Mg₂Ni is considered to be formed by the reaction of Mg and Ni during hydriding-dehydriding cycling and has higher hydriding and

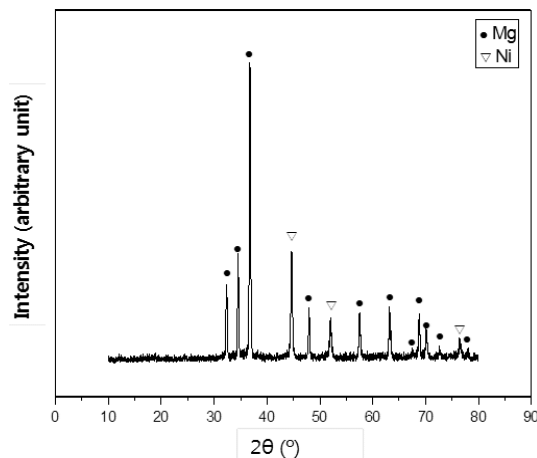


Fig. 7 XRD pattern of Mg-23.5Ni after reactive mechanical grinding

dehydriding rates than Mg. During hydriding-dehydriding cycling, hydriding and dehydriding reactions of both Mg and Mg₂Ni phases occur under our experimental conditions.

Fig. 1 and Fig. 3 showed that activated Mg-Ni has a lower hydriding rate and a lower H_a value after 60 min, compared with Mg-23.5wt%Ni heat-treated after melt spinning¹⁸⁾. The nonhomogeneous distribution of Ni particles in the mixture and the larger sizes of the particles in the Mg-Ni alloy are considered to lead to the lower hydriding rate and the lower H_a value after 60 min. The Mg-Ni alloy has the hydriding rate for 5 min of 0.186 wt%/min and the H_a after 60 min of 1.42 wt% at 593K under 12 bar H₂.

The RMG of Mg with Ni is considered to facilitate nucleation by creating many defects on the surface and in the interior of Mg and by the action of the additives themselves as active sites for the nucleation, and shorten diffusion distances of hydrogen atoms by reducing the particle size of Mg.

Created defects and cracks, and the fragmentation into fine particles, due to the expansion and con-

traction of the hydride - forming materials (Mg and Mg₂Ni) with the hydriding and dehydriding reactions, are also considered to increase the hydriding and dehydriding rates of the mixture.

Activation was completed only after two hydriding-dehydriding cycles at 593K for the Mg-23.5Ni sample. Hydriding and dehydriding reactions were performed under 12 bar H₂ and 1.0 bar H₂, respectively. Reactive mechanical grinding for 4 h in a planetary ball mill is considered to lead to the completion of the activation in a small number of hydriding-dehydriding cycles.

4. Conclusions

The activated 76.5wt%Mg - 23.5wt%Ni (Mg-23.5Ni) has a lower hydriding rate, compared with Mg-23.5wt%Ni heat-treated after melt spinning, due to the nonhomogeneous distribution of Ni particles in the mixture and the larger sizes of the particles. Activation of the Mg-23.5Ni sample was completed only after two hydriding (under 12 bar H₂) - dehydriding (under 1.0 bar H₂) cycles at 593K. The reactive mechanical grinding of Mg with Ni is considered to facilitate nucleation and shorten diffusion distances of hydrogen atoms. After hydriding - dehydriding cycling, the Mg-23.5Ni sample contained Mg₂Ni phase. During hydriding - dehydriding cycling, hydriding and dehydriding reactions of both Mg and Mg₂Ni phases occurred under our experimental conditions.

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