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Development of Mg-10wt.%Ni Hydrogen-Storage Alloy by Mechanical Alloying

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기계적인 합금에 의한 Mg-10wt.%Ni 수소저장합금의 개발

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초 록

순수한 Mg의 수소와의 반응속도를 증가시키기 위하여 기계적으로 합금처리한 Mg-10wt.%Ni 혼합물의 수소화물 형성·분해 성질을 조사하였다. 수소화물 형성·분해 cycling을 시킴에 따라 Mg_2Ni상이 형성되고 그 양이 증가한다. 기계적인 합금 처리와 수소화물 형성·분해 cycling의 주요 효과는 결함의 수를 증가시키고, 비표면적을 크게하는 것으로 생각된다. 기계적으로 합금처리한 Mg-10wt.%Ni 혼합물은 활성화가 용이하게 이루어지고, 순수한 Mg, Mg-10wt.%Ni합금, Mg-25wt.%Ni합금, 그리고 Mg_2Ni합금과 비교하여, 수소화물 형성 속도와 수소 저장 용량이 아주 크고, 수소화물 분해 속도가 비교적 높다.

Abstract

The hydriding and dehydriding properties of a Mg-10wt.%Ni mixture, mechanically-alloyed in order to improve the hydriding and dehydriding kinetics of pure Mg, were investigated. The Mg_2Ni phase develops along with

hydriding-dehydriding cycling. The principal effects of mechanical alloying in a planetary mill and hydriding-dehydriding cycling are considered to be the augmentation in the density of defects and the enlargement in the specific surface area. The mechanically-alloyed Mg-10wt.%Ni mixture is activated easily. It has much higher hydriding rate and hydrogen-storage capacity and relatively high dehydriding rate as compared with the pure Mg, the Mg-10wt.%Ni alloy, the Mg-25wt.%Ni alloy and the Mg_2Ni alloy.

1. Introduction

Magnesium has many advantages for a hydrogen storage material; large hydrogen storage capacity(7.6wt%), low cost and abundance in the Earth's crust. But its hydriding and dehydriding kinetics are very slow[1]. Much work to ameliorate the reaction kinetics of magnesium with hydrogen has been carried out by alloying certain metals with magnesium[2-9], by mixing metal additives with magnesium[10], by plating nickel on the surface of magnesium[11] and by synthesizing magnesium hydride in the presence of a homogeneous catalyst[12]. In particular, the Mg/Ni-H_2 system has been studied by alloying[3, 13-16] and by plating[11].

In this work we tried to improve the reaction kinetics of magnesium with hydrogen by mechanical alloying of magnesium with nickel. The hydriding and dehydriding properties of a mechanically-alloyed mixture with a composition Mg-10wt.%Ni was investigated and they were compared with the hydrogen-storage properties of the Mg_2Ni alloy, the pure Mg and the magnesium-rich alloys with similar compositions reported earlier.

2. Experimental

The purity of hydrogen employed was 99.99%. Magnesium and nickel powder mixtures(about 3 g) with a composition Mg-10wt.%Ni were mechanically alloyed under an argon atmosphere in a planetary mill for 5 min. X-ray diffraction patterns of the prepared mixtures showed only magnesium and nickel.

Fig.1 shows schematically the Sievert's type hydriding and dehydriding apparatus made of stainless steel pipe. This apparatus consists of three parts ; gas(H_2, Ar)cylinders, standard volume and reactor. Ar gas is used for measuring the dead volume of each part and for controlling the atmosphere during heating the reactor to reaction temperatures. The pressures in the standard volume and the reactor are read by a pressure gauge(P.G.) and a pressure transducer(P.T.) connected to the strip-chart recorder, respectively. The dead volume of the part for the standard volume with the pressure transducer is

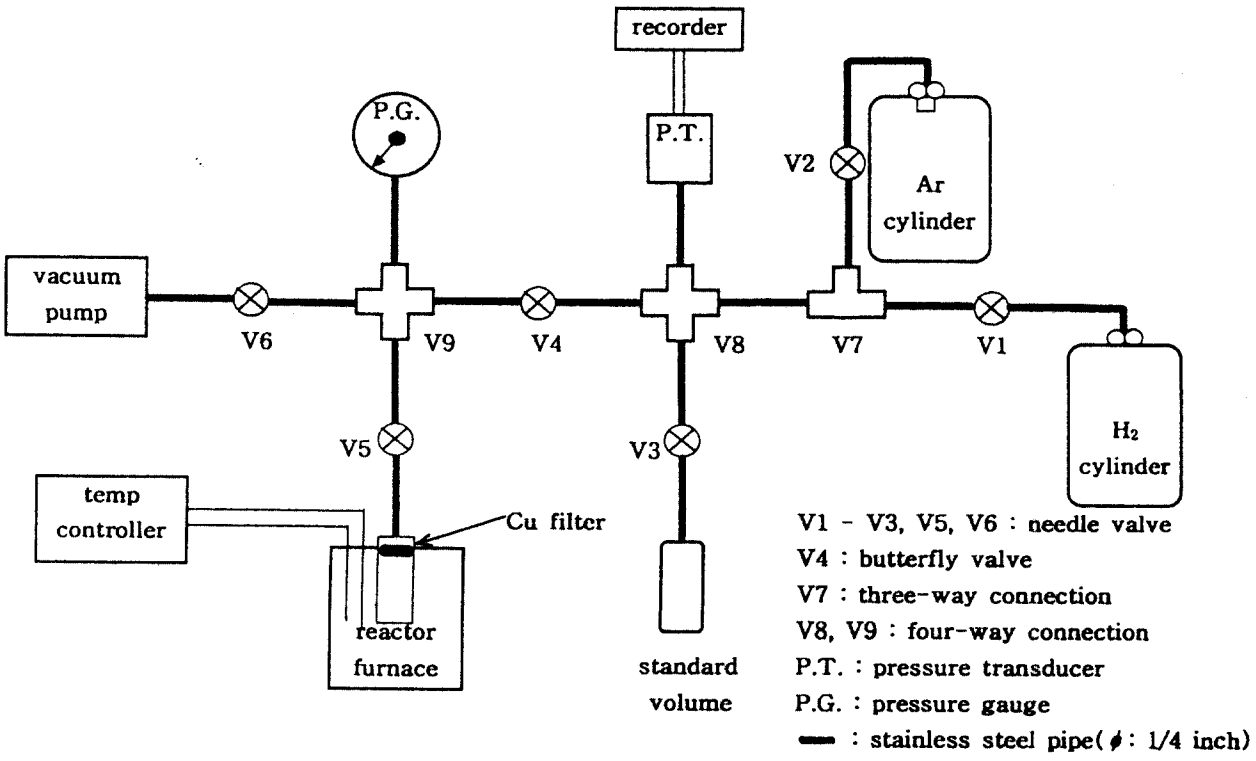

Fig.1 Scheme of the hydriding and dehydriding apparatus.

$123.7cm^3$, and that of the part for the reactor with the pressure gauge is $31.1cm^3$. A Cu-filter(made by sintering Cu powder) is inserted in the head of the reactor in order to prevent the sample powder from being pumped out during the operation of vacuum pump. The hydrogen pressures were maintained nearly constant during the hydriding and dehydriding reaction by dosing or taking out an appropriate quantity of hydrogen with a butterfly value V_4. The variation of the hydrogen pressure in the part of the standard volume permits one to calculate the quantity of hydrogen absorbed or desorbed by the sample as a function of time.

3. Results and Discussions

H_a is defined as the weight percentage of absorbed hydrogen with respect to the sample weight. In Fig.2 are shown the variations of H_a(wt.%) of a mechanically-alloyed Mg-10wt.%Ni mixture as a function of time t(min) at 573 K, 7 bar H_2 according to the number of hydriding-dehydriding cycles n. The amount of the sample used was about 0.44g. The H_a vs. t curves for n=5, 6 and 7 are nearly superimposed. This indicates that the activation of the mechanically-alloyed Mg-10wt.%Ni mixture is completed after about five hydriding-dehydriding cycles.

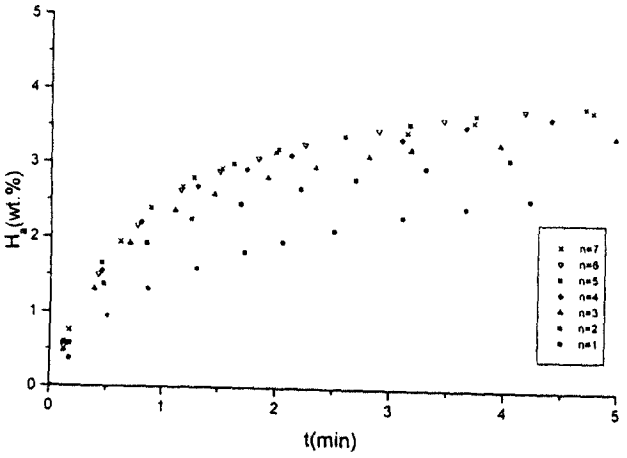

Fig.2 H_a vs. t curves at 573 K, 7 bar H_2 according to the number of hydriding-dehydriding cycles n.

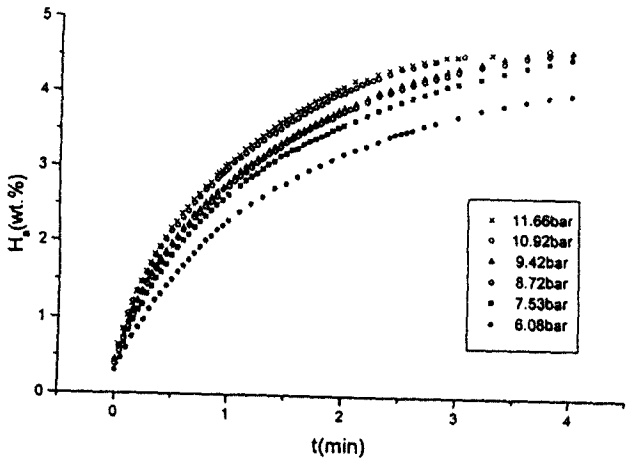

Fig.3 H_a vs. t curves of the activated Mg-10wt.%Ni mixture at 575 K under 6.08-11.66 bar H_2.

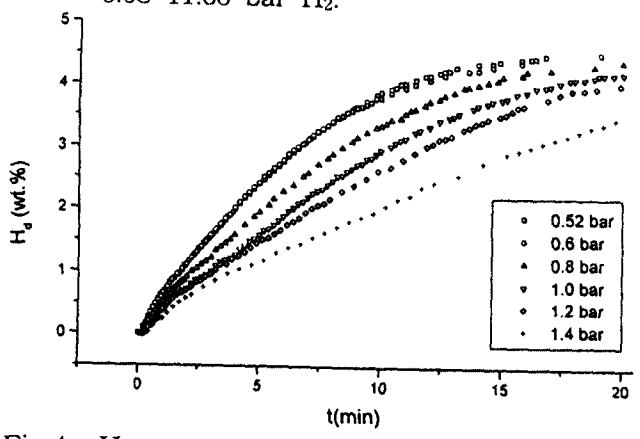

Fig.4 H_d vs. t curves of the activated Mg-10wt.%Ni mixture at 575K under 0.52-1.4 bar H_2.

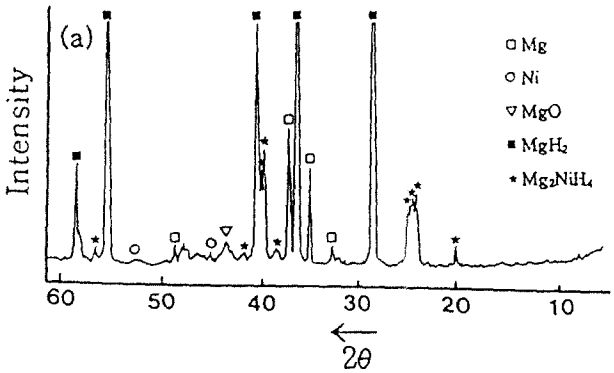

Fig.5 X-ray(Cu k_α) powder diffraction pattern of the Mg-10wt.%Ni mixture hydrided at 583K, 8 bar H_2 after 11 hydriding-dehydriding cycles.

Fig.3 shows the H_a vs. t curves of the activated Mg-10wt.%Ni mixture at 575K under the hydrogen pressures between 6.08 bar and 11.66 bar. The amount of the sample used was about 0.45 g. The H_a under 11.66 bar H_2 is about 4.60 wt.% after 4 min.

We define H_d as the weight percentage of desorbed hydrogen with respect to the sample weight. In Fig.4 are shown the variations of H_d(wt.%) of the activated Mg-10wt.%Ni mixture as a function of time t(min) at 575 K according to the number of hydriding-dehydriding cycles n. The amount of the sample used was about 0.45 g. The H_d vs. t curves exhibit two distinct stages. The H_d under 0.52 bar H_2 is about 4.53 wt.% after 20 min.

Fig.5 shows an X-ray(Cu K_α) powder diffraction pattern of the Mg-10wt.%Ni mixture hydrided at 583K, 8 bar H_2 after 11 hydriding-dehydriding cycles. The sample contains Mg_2NiH_4, MgH_2, Mg and Ni phases with a small quantity of MgO. Under the experimental conditions for

the hydriding reaction in Fig.2 and Fig.3, both Mg_2Ni hydride and Mg hydride form. Under the experimental conditions for the H_d vs. t curves in Fig.4, both Mg_2Ni hydride and Mg hydride decompose. The dehydriding rate of Mg_2Ni hydride is known higher than that of Mg hydride. The first stage in the H_d vs. t curves in Fig.4 is considered to correspond mainly to the decomposition of the Mg_2Ni hydride.

Fig.6 shows the microstructures observed by scanning electron microscope(SEM) of the Mg-10wt.%Ni mixture before and after hydriding cycling. Fig.6(a), (b) and (d) show topographies, and Fig.6(c) gives a chemical map by back-scattered electrons showing the distribution of nickel. Nickel is represented as white points on the chemical map. Fig.(b) and (c) are the microstructures of the cross-section of

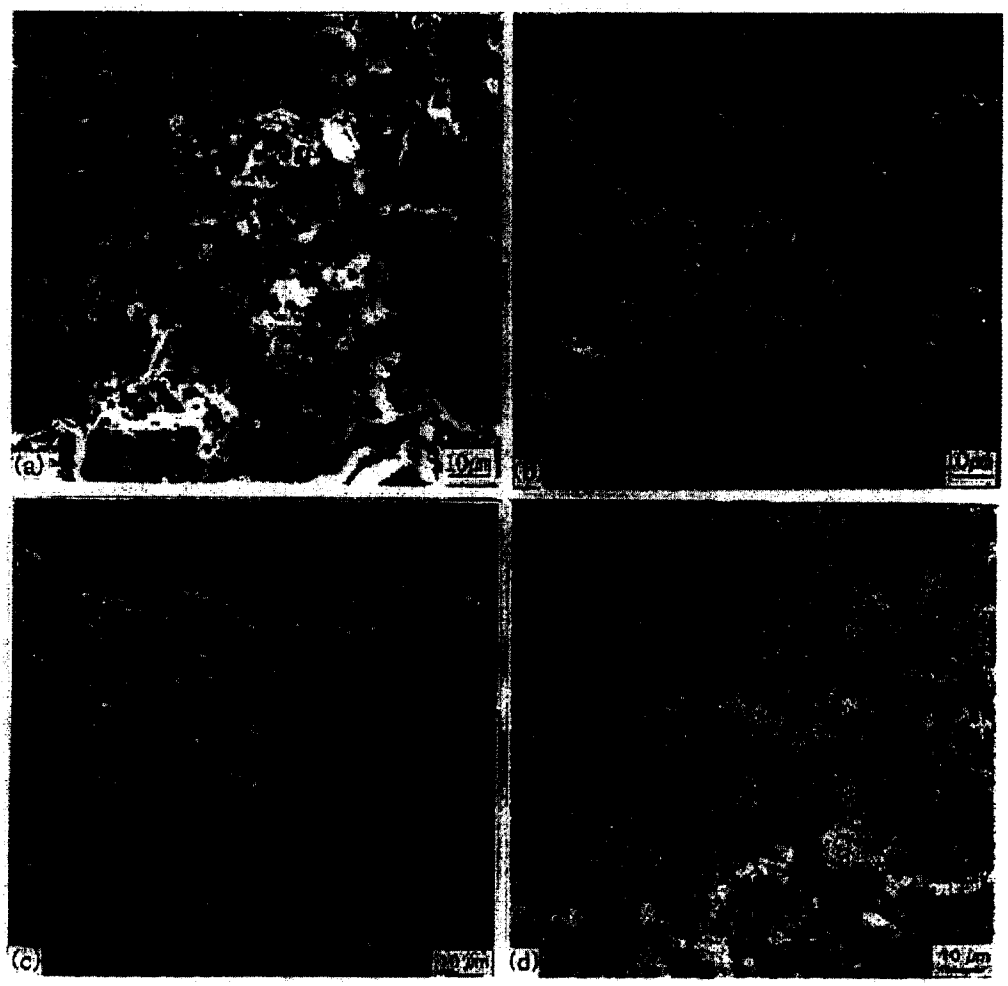

Fig.6 Microstructures observed by SEM of the Mg-10wt.%Ni mixture before and after hydriding cycling: (a) topography, n=0 ; (b) topography(cross-section), n=0 ; (c) distribution of nickel (cross-section), n=0 ; (d) topography, n=7.

chemical map. Fig.(b) and (c) are the microstructures of the cross-section of the sample. The mechanically-alloyed Mg-10wt.%Ni mixture contains many defects, and the nickel is distributed in parallel and discontinuous lines. Fig.6(d) shows that the particles became very fine after hydriding-dehydriding cycling.

The principal effects of mechanical alloying by a planetary mill are considered to be enlargement in the specific surface area and augmentation in the number of defects on the surface as well as in the interior of the materials. The expansion and contraction of the lattice during hydriding-dehydriding cycling favors the diminution of particle size and can create numerous defects. On the contrary the annealing effect during hydriding-dehydriding cycling can bring about the diminution of specific surface area by sintering and the decrease in the number of defects.

The defects created on the surface and in the interior of the materials and/or Ni and Mg_2Ni(or Mg_2Ni hydride)formed during hydriding-dehydriding cycling, can be nucleation sites for the Mg_2Ni hydride and/or the Mg hydride.

In Fig.7 are given the hydriding curves of the mechanically-alloyed Mg-10wt.%Ni mixture (0.44g) and the Mg_2Ni alloy(0.90g) at 573 K, 7 bar H_2, together with those of the Mg-10wt.%Ni alloy at 582 K, 9 bar H_2[17], and the pure Mg at 675 K, 30 bar H_2[18] reported earlier. The mechanically-alloyed Mg-10wt.%Ni mixture [Mg-10wt.%Ni(M.A.)] shows much higher hydriding rate and

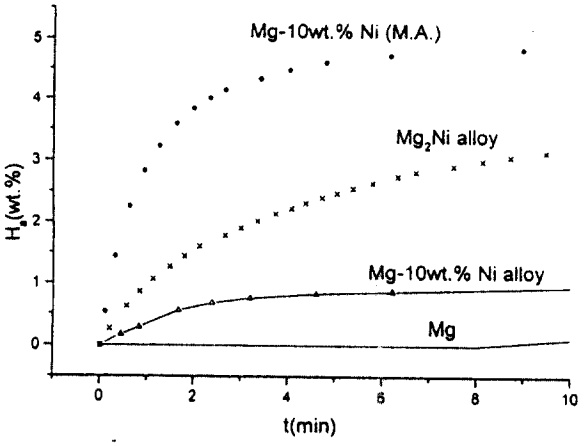

Fig.7. Hydriding curves of the mechanically-alloyed Mg-10wt.%Ni mixture [Mg-10wt.%Ni(M.A.)], the Mg_2Ni alloy, the Mg-10wt.%Ni alloy and the pure Mg.

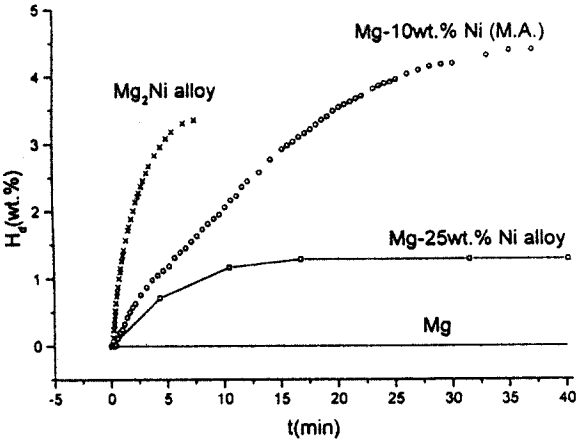

Fig.8 Dehydriding curves of the mechanically-alloyed Mg-10wt.%Ni mixture [Mg-10wt.%Ni(M.A.)], the Mg_2Ni alloy, the Mg-25wt.%Ni alloy and the

hydrogen-storage capacity than the pure Mg and the other alloys.

Fig.8 shows the dehydriding curve of the mechanically-alloyed Mg-10wt.%Ni mixture (0.45g) at 575 K, 1.4 bar H_2, together with those of the Mg_2Ni alloy(0.78g) at 576 K, 1.4 bar H_2[19], the Mg-25wt.%Ni alloy at 618K under vacuum[4] and the pure Mg at 595 K, 1.5

bar H_2[20] reported earlier. The Mg_2Ni alloy has the highest dehydriding rate, but it has lower hydrogen-storage capacity than the mechanically-alloyed Mg-10wt.%Ni mixture. The Mg-10wt.%Ni(M.A.) exhibits much higher dehydriding rates than the pure Mg and the Mg-25wt.% alloy.

4. Conclusions

The hydriding and dehydriding properties of a mechanically-alloyed mixture with a composition Mg-10wt.%Ni was investigated and the following conclusions were drawn:

The Mg_2Ni phase develops in the mechanically-alloyed Mg-10wt.%Ni mixture along with hydriding-dehydriding cycling.

The principal effects of mechanical alloying in a planetary mill and hydriding-dehydriding cycling are the augmentation in the density of defects and the enlargement in the specific surface area. The former facilitates the nucleation of the Mg and Mg_2Ni hydrides and α-solid solution of Mg_2Ni and/or Mg, and the latter shortens the diffusion distance of hydrogen in the hydriding and dehydriding reactions.

The mechanically-alloyed Mg-10wt.%Ni mixture is easily activated and shows much higher hydriding rate and hydrogen-storage capacity than the pure Mg, the Mg-10wt.%Ni alloy and the Mg_2Ni alloy.

The mechanically-alloyed Mg-10wt.%Ni mixture shows lower dehydriding rate than the Mg_2Ni alloy but higher dehydriding rate than the pure Mg and the Mg-25wt.% alloy.

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