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기계적 합금처리된 2Mg+Ni 혼합물의 수소 저장 특성에 관한 연구

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A Study on the Hydrogen-Storage Characteristics of a Mechanically-Alloyed 2Mg+Ni Mixture

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Abstract

A mixture with a composition Mg_2Ni is mechanically alloyed. Its hydriding and dehydriding properties are compared with those of the intermetallic compound Mg_2Ni prepared by partial melting and sintering. The principal effects of mechanical alloying in a planetary mill and hydriding-dehydriding cycling are considered the enlargement in the specific surface area and the augmentation in the density of defects.

1. Introduction

The intermetallic compound Mg_2Ni is considered as an appropriate material for hydrogen storage from the viewpoint of hydrogen storage capacity(about 3.7 wt.%), hydride stability[1,2], and hydriding and dehydriding kinetics[3-10]. However, the process for the preparation of Mg_2Ni is not simple[7-10].

In this work, a mixture of magnesium and nickel with a composition Mg_2Ni is mechanically alloyed. Its hydriding and dehydriding properties are investigated, and are compared with those of the intermetallic compound Mg_2Ni prepared by partial melting and sintering.

2. Experimental

Mechanical alloying of Mg with Ni (with the composition Mg_2Ni) was achieved in a planetary mill (acceleration about 60 ms^{-2}). We used alfa Mg and "carbonyl-type" Ni (3-5μm particles). 3g of this mixture together with 200g of stainless steel balls(4mm) were stirred in a planetary mill under argon for 30 min. The resulting samples can contain 0.5-1 % Fe. X-ray diffraction patterns were used for the identification of phases. A Sievert's type hydriding apparatus[11] was employed for the measurements of hydriding rates. It consists of a standard volume and a reactor. They are linked to Bourdon gauges which permit measuring the pressure from 0 to 10 bar with a precision of 0.05 bar. The hydrogen pressure was maintained nearly constant during the hydriding reaction by dosing a quantity of hydrogen from the standard volume to the reactor. The dosed quantity of hydrogen is the hydrogen quantity which is absorbed by the sample between the measurements for the quantities of absorbed hydrogen. For dehydriding kinetics, the quantities of desorbed hydrogen were measured as a function of time by volumetry with an apparatus whose running is semi-automatic[8].

3. Results and Discussion

Fig.1 shows x-ray diffraction pattern of the mechanically-alloyed mixture dehydrided after 12 hydriding-dehydriding cycles between 0 and 7 bar H_2 at 573 K (for 14 days). The diffraction pattern exhibit Mg_2Ni, Mg, Ni and MgO phases.

Figure 2(a) shows hydrided fraction (F) vs. time (t) curves for the mechanically-alloyed 2Mg+Ni mixture(0.89g) according to the number of hydriding cycles (n) at 573 K under 7 bar H_2. The hydrided fraction F is defined as following:

F ≡ number of H_2 moles absorbed during t min / number of H_2 moles calculated on the assumption that 100% of the sample is hydrided into the composition Mg_2NiH_4.

This definition of F allows us to compare the hydriding characteristics of the mechanically alloyed 2Mg+Ni mixture with those of the Mg_2Ni alloy prepared by partial melting and sintering.

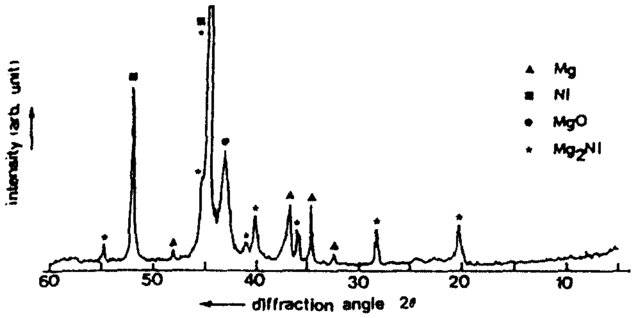

Fig.1 X-ray diffraction pattern of the mechanically-alloyed 2Mg+Ni mixture dehydrided after 12 hydriding-dehydriding cycles between 0 and 7 bar H_2 at 573 K (for 14 days).

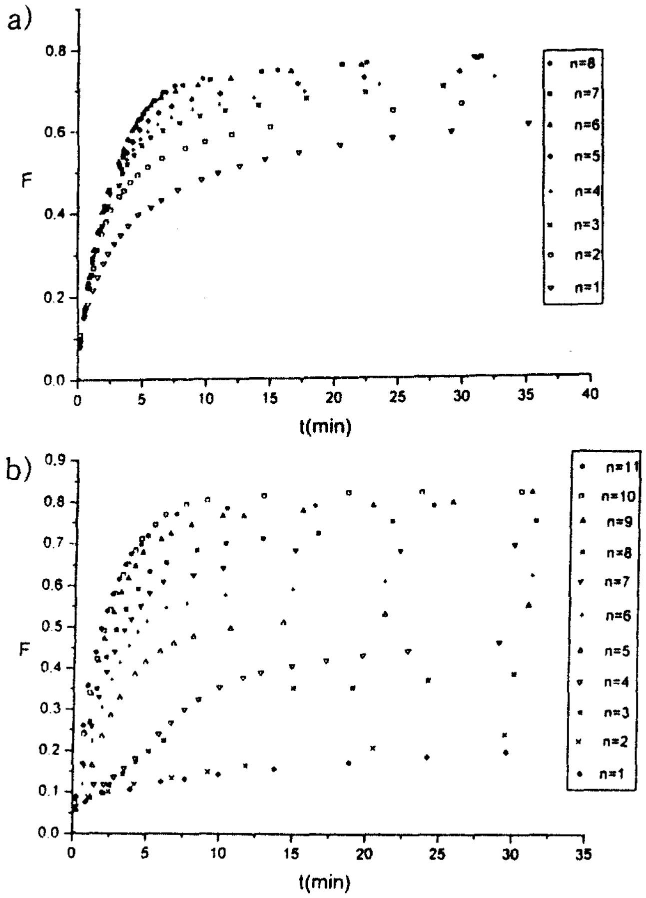

Fig.2 Hydrided fraction (F) vs. time (t) curves according to the number of hydriding cycles (n) at 573 K under 7 bar H_2 (a) for the mechanically-alloyed 2Mg+Ni mixture (0.89g) and (b) for the Mg_2Ni alloy (0.60g).

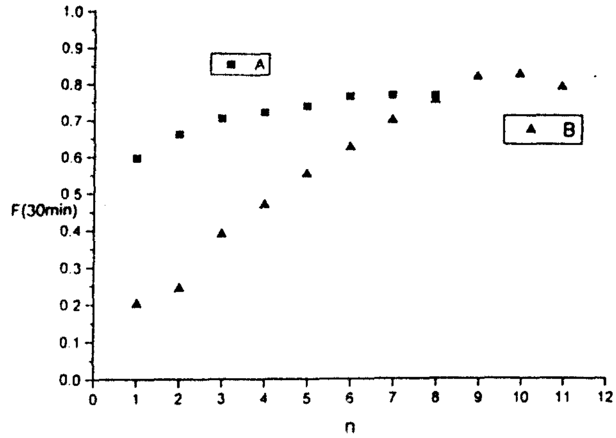

Fig.3 Hydrided fractions F (30 min) obtained after 30 min under 7 bar H_2 at 573 K according to the number of hydriding cycles(n) for the mechanically-alloyed 2Mg+Ni mixture (A) and for the Mg_2Ni alloy (B).

When the mixture 2Mg+Ni is heated (to 573K in our experimental condition of activation for hydriding), some of the mixture is considered to form Mg_2Ni phase:

$$2Mg + Ni \rightarrow Mg_2Ni. \quad (1)$$

In the first hydriding cycle the following reactions are considered to take place in our experimental conditions:

$$Mg + H_2 \rightarrow MgH_2 \quad (2)$$

$$Mg_2Ni + 2H_2 \rightarrow Mg_2NiH_4 \quad (3)$$

$$2Mg + Ni + 2H_2 \rightarrow Mg_2NiH_4 \quad (4)$$

As the number of the hydriding cycles increases and consequently the period of annealing becomes longer, the reaction (3) will be dominant.

Fig.2(b) shows the F vs. t curves for the Mg_2Ni prepared by partial melting and sintering(0.60g) according to n at 573 K under 7 bar H_2.

Fig.3 shows the hydrided fractions F(30 min) obtained after 30 min under 7 bar

H_2 at 573K according to the number of hydriding cycles n for the mechanically-alloyed 2Mg + Ni mixture (A) and for the Mg_2Ni alloy (B). Already in the first hydriding cycle the mechanically-alloyed material gives F=0.60 after 30 min whereas the Mg_2Ni alloy prepared by partial melting and sintering shows only F=0.2 in the same experimental conditions. The excellent hydrogen absorption rate during activation period of the mechanically-alloyed Mg_2Ni is considered as resulting from the increase of the reaction surface area due to the mechanical mixing and milling. The activation of the mechanically-alloyed 2Mg + Ni mixture is accomplished after about 6 hydriding cycles and that of the Mg_2Ni alloy prepared by partial melting and sintering after about 9 hydriding cycles. The mechanically-alloyed mixture has a little smaller hydrogen storage capacity than the Mg_2Ni alloy just after activation.

The nickel transformed into Mg_2Ni was about 73%. For this analysis, the mechanically-alloyed mixture hydrided under 8 bar H_2 at 583K (under these conditions, both Mg_2Ni and Mg can be hydrided), and then dehydrided under 2.5 bar H_2 at 583K for the decomposition of the Mg_2Ni hydride alone. The mechanically-alloyed mixture contains Mg_2Ni, Mg, Ni and MgO phases. The hydriding rate of Mg is known to be low. The lower fraction of Mg_2Ni and the lower hydriding rate of Mg in the mechanically-alloyed mixture lead probably to a little smaller hydrogen-storage capacity than the Mg_2Ni alloy just after activation.

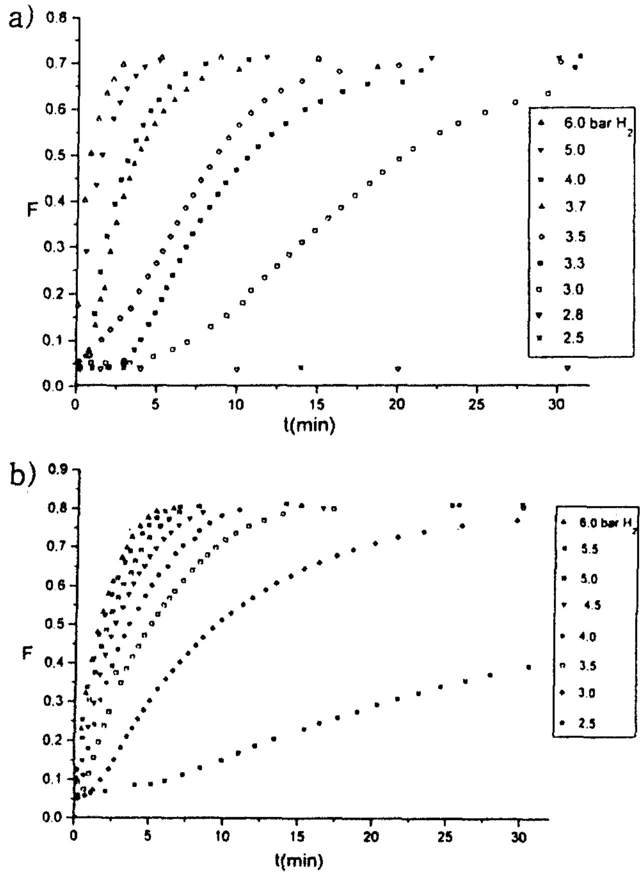

Fig.4 Hydrided fraction (F) vs. time (t) curves under 2.5-6.0 bar H_2 (a) for the mechanically-alloyed mixture at 543 K and (b) for the Mg_2Ni alloy at 548 K.

Fig.4(a) shows the F vs. t curves for the mechanically-alloyed mixture at 543 K under 2.5-6.0 bar H_2. They exhibit at the very beginning an extremely rapid hydrogen absorption up to F~0.05. Then some of them show incubation periods. It is considered that the region from F=0 to F~0.05 corresponds to non-saturated α-solid solutions(Mg_2Ni-H and Mg-H solid solutions). After this initial period the actual hydriding reaction begins. Fig.4(b) shows the F vs. t curves for the Mg_2Ni alloy prepared by partial melting and sintering at 548 K under 2.5-6.0 bar H_2. They also exhibit at the very beginning an extremely rapid hydrogen absorption up to $F \sim 0.05$. The mechanically-alloyed mixture shows hydriding rates similar to those of the Mg_2Ni alloy.

We define dehydrided fraction F' at time t(min) as the number of moles of H_2 desorbed during t(min) divided by the number of moles of H_2 absorbed before the dehydriding measurement.

Fig. 5(a) shows the curves of the hydrided fraction F' vs. time t for the dehydriding reaction of the mechanically-alloyed mixture at 586 K under 1.4-1.8 bar H_2. A short incubation period of about 0.1 min is observed under 1.8 bar H_2. This is considered as resulting from a slow nucleation of the α-solid solutions of Mg_2Ni and/or Mg in those experimental conditions.

Fig.5(b) shows the F' vs. t curves for the dehydriding reaction of the Mg_2Ni alloy prepared by partial melting and sintering at 585 K under 1.4-1.8 bar H_2. A short incubation period of about 0.08 min is observed under 1.8 bar H_2.

Fig.6 shows the microstructure of the mixture mechanically-alloyed during 5 min. The mechanically-alloyed mixture has many cracks and defects.

The principal effects of mechanical alloying by planetary mill are considered to be enlargement in 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.

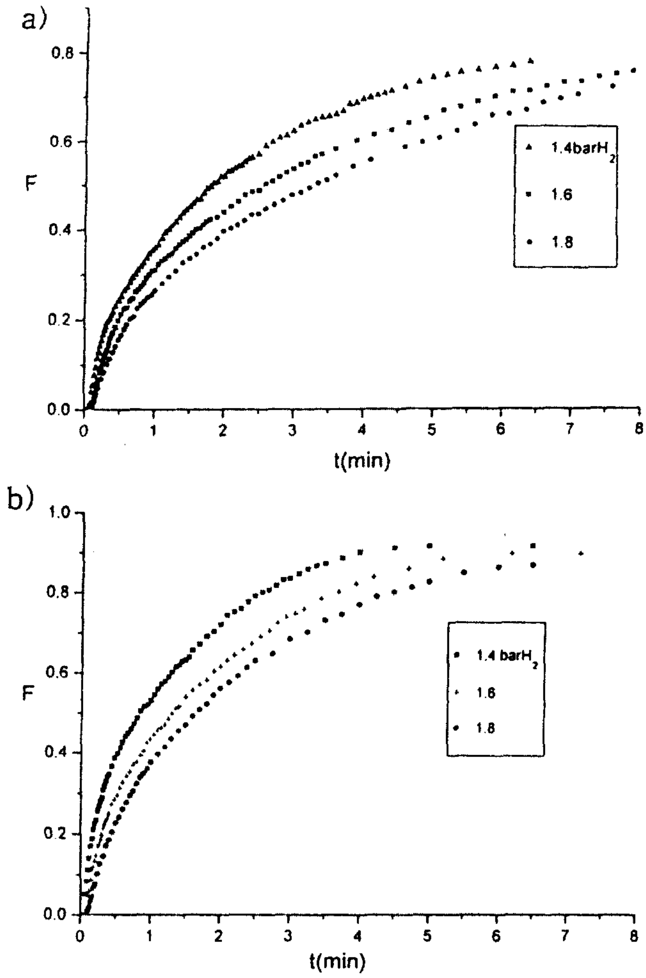

Fig.5 Dehydrided fraction (F') vs. time (t) curves under 1.4-1.8 bar H_2 (a) for the mechanically-alloyed mixture at 586 K and (b) for the Mg_2Ni alloy at 585 K.

On the contrary the annealing effect during hydriding-dehydriding cycling can bring about the diminution of specific surface area by sintering and decrease the number of defects. The enlargement in the specific surface area decreases the effective particle size, shortening the diffusion distance of hydrogen in the hydriding and dehydriding reactions. The defects can be active nucleation sites for the hydrides and the α-solid solutions of Mg_2Ni and/or Mg.

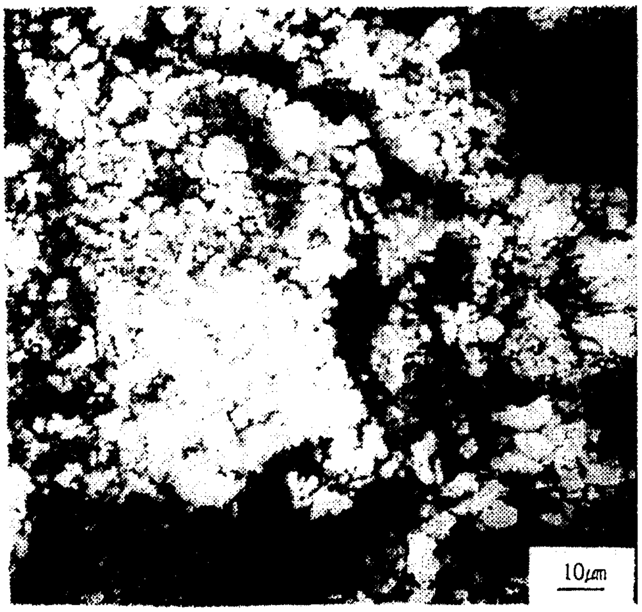

Fig.6 Microstructure of the 2Mg + Ni mixture alloyed mechanically during 5min.

4. Conclusions

The principal effects of mechanical alloying in a planetary mill and hydriding-dehydriding cycling are the enlargement in the specific surface area and the augrnentation in the density of defects.

As compared with the Mg_2Ni alloy prepared by partial melting and sintering,

- the mechanically-alloyed mixture with a similar composition has a little smaller hydrogen storage capacity just after activation.
- the preparation of the material is much easier.
- the activation of the material for hydriding is easier.
- its hydriding rates and dehydriding rates are similar.

Acknowledgement

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