Hydrogen Absorption by Mg-Ni-Fe₂O₃ and Mg-Ni-Ti during Mechanical Grinding under Hydrogen

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Abstract: Samples with compositions of 80 wt% Mg-14 wt% Ni-6 wt% Fe₂O₃ and 80 wt% Mg-14 wt% Ni-6 wt% Ti were prepared by mechanical grinding under hydrogen (reactive mechanical grinding). Their hydrogen absorptions during reactive mechanical grinding were examined. TGA and BET analysis were employed to investigate the hydrogen storage properties of the prepared alloys. TGA analysis of the Mg-14Ni-6Fe₂O₃ showed an absorbed hydrogen quantity of 6.91 wt% while that of Mg-14Ni-6Ti was 2.59 wt%. BET analysis showed that the specific surface area of Mg-14Ni-6Fe₂O₃ and Mg-14Ni-6Ti after reactive mechanical grinding were 264 m²/g and 64 m²/g, respectively. The larger absorbed hydrogen quantity and the larger specific surface area of Mg-14Ni-6Fe₂O₃ after RMG than those of Mg-14Ni-6Ti after RMG showed that the effects of Fe₂O₃ addition are much stronger than those of Ti addition during reactive mechanical grinding.

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Keywords: Hydrogen absorbing materials, mechanical alloying/milling, microstructure, scanning electron microscopy (SEM), Fe₂O₃ or Ti addition.

1. INTRODUCTION

Excess alternative energies such as wind, solar, tidal or geothermal energy can be used to produce hydrogen. When hydrogen is converted into energy by a reaction with oxygen, water is the only exhaust product. So, it does not cause environmental contamination as an energy carrier.

Metal hydrides can store more hydrogen per unit volume, and is safer than other hydrogen storage methods such as pressure storage and cryogenic storage. It can also use waste heat to release hydrogen.

Magnesium has many advantages as a hydrogen storage material, but its reaction rates with hydrogen are very low [1]. Many works to improve the hydriding and dehydriding rates of magnesium have been carried out by alloying with magnesium certain metals such as Cu [2], Ni [3,4], and In [5], by synthesizing compounds such as CeMg₈ [6] and MgₓTi₁₋ₓFe₁₋ₓNiₓ (x = 4,8) [7], and by making compo-

sites such as Mg-20 wt% Fe₃Y₈ [8], Mg-20 wt% Ni-Y [9], Mg-Sn [10], and Mg-V [11]. To improve the reaction rates of Mg with H₂, Aminorroaya et al. [12] added Nb and multi-walled carbon nanotubes to Mg-Ni alloys, and Cho et al. [13] added transition metals to cast Mg-Ni alloys. Milanese et al. [14] mixed Ni and Cu with Mg, Tanguy et al. [15] mixed metal additives with magnesium, and Eisenberg et al. [16] plated nickel on the surface of magnesium to improve the hydriding-dehydriding kinetics of MgH₂.

The magnesium prepared by mechanical grinding under H₂ (reactive mechanical grinding) with transition elements or oxides showed relatively high reaction rates with hydrogen when the additive content was about 20 wt%.

Reilly et al. [3] and Akiba et al. [4] improved the reaction kinetics of Mg with H₂ by preparing Mg-Ni alloys. Song et al. [17-20] increased the hydriding and dehydriding rates of Mg by mechanical alloying of Mg with Ni under Ar atmosphere. Bobet et al. [21] improved the hydrogen-storage properties of both magnesium and Mg + 10 wt% Co, Ni,
or Fe mixtures by reactive mechanical grinding for a short time (2 h). We chose Ni as a transition element to be added. Ti was also selected since it was reported to increase the hydriding and dehydriding rates when it was added [22,23].

Hydriding rate of Mg was greatly improved by the addition of FeO prepared by spray conversion via reactive mechanical grinding [24]. But the preparation of FeO by spray conversion requires complicated processes. We thus used purchased FeO to prepare the samples. An addition of too much FeO will decrease the hydrogen storage capacity. We added less than 6 wt% to get a high effect of the oxide addition without decreasing the hydrogen storage capacity severely.

In this work, samples with compositions of 80 wt% Mg-14 wt% Ni-6 wt% FeO and 80 wt% Mg-14 wt% Ni-6 wt% Ti were prepared by reactive mechanical grinding. Their hydrogen absorptions during reactive mechanical grinding were examined. We designated 80 wt% Mg-14 wt% Ni-6 wt% FeO and 80 wt% Mg-14 wt% Ni-6 wt% Ti as Mg-14Ni-6FeO and Mg-14Ni-6Ti, respectively.

2. EXPERIMENTAL PROCEDURES

Pure Mg powder (particle size 297–100 μm, purity 99%, Fluka), Ni (average particle size ~5 μm, purity 99.9%, Ceracon), FeO (average particle size < 5 μm, purity ≥ 99%, Aldrich), and Ti (~44 μm, purity 99.9%, Aldrich) 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 (volume of 250 ml) was then filled with high purity hydrogen gas (about 12 bar). The reactive mechanical grinding was performed for 6 h (milling 2 h + refilling with H2 + milling 2 h + refilling with H2 + milling 2 h).

The absorbed or desorbed hydrogen quantity was measured as a function of time by a volumetric method, using Sievert’s type hydriding and dehydriding apparatus described previously [25]. 0.5 g of the samples was used for the measurement of the absorbed or desorbed hydrogen quantity as a function of time. The microstructures were observed by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

Figure 1 shows TGA curves at 373-673 K for Mg-14Ni-6FeO and Mg-14Ni-6Ti after reactive mechanical grinding. The weight in the curve for Mg-14Ni-6FeO decreases slowly from 373 K, and then decreases rapidly from about 473 K to about 583 K. The weight in the curve for Mg-14Ni-6Ti decreases very slowly from 373 K, and then decreases rapidly from about 473 K to about 513 K. Mg-14Ni-6FeO and Mg-14Ni-6Ti exhibit decreases of 6.91 and 2.59 wt%, respectively. The increases in the weights of samples after decrease in the sample weights are due to buoyancy effect, a phenomenon that weight seems to increase since the gas density decreases as temperature rises.

BET graphs [1/V(Vo/P-1)] vs. P/Po plots for Mg-14Ni-6FeO and Mg-14Ni-6Ti after reactive mechanical grinding are presented in Fig. 2 where V is the volume of adsorbed gas, P is the saturated pressure of adsorbed gas, and P is the equilibrium pressure of adsorbed gas. According to BET equation the specific surface area is large when the plot 1/{V(2/P)} vs. P/Po has a small slope and a small value of intercept on the vertical axis. The plots show that Mg-14Ni-6FeO has a larger specific surface area than Mg-14Ni-6Ti. The specific surface areas of Mg-14Ni-6FeO