Hydrogen Storage Properties of a Ni and NbF₅-added Mg Alloy

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Abstract: Samples with a composition of 80 wt% Mg-14 wt% Ni-6 wt% NbF₅ (denoted as Mg-14Ni-6NbF₅) were prepared by reactive mechanical grinding, and the hydriding and dehydriding properties of the specimens were then examined. The activation of Mg-14Ni-6NbF₅ was completed after two hydriding (under 12 bar H₂)–dehydriding (in vacuum) cycles. Mg-14Ni-6NbF₅ had a hydrogen storage capacity of about 5.5 wt% H. At the number of cycles n = 2, the sample absorbed 4.93 wt% H for 5 min, 5.20 wt% H for 10 min, and 5.48 wt% H for 60 min at 573 K under 12 bar H₂, and desorbed 0.58 wt% H for 10 min, 1.52 wt% H for 30 min, and 2.47 wt% H for 60 min at 573 K under 1.0 bar H₂. The hydriding rate increased as the temperature increased from 423 K to 573 K since the effect of acceleration of thermally activated process predominates, and decreased from 573 K to 623 K since the effect of decrease in the driving force for the hydriding reaction predominates. NbF₅ formed MgF₂ and NbH₂ by the reaction with Mg and hydrogen. Mg-14Ni-6NbF₅ exhibited a higher hydriding rate than both Mg-10NbF₅ and Mg-14Ni-6Fe₂O₃.

(Received November 21, 2012)

Keywords: hydrogen absorbing materials, mechanical alloying/milling, scanning electron microscopy (SEM), X-ray diffraction, Ni and NbF₅ addition

1. INTRODUCTION

Compared with other hydrogen storage methods such as pressure storage, cryogenic storage, and carbon nanotube storage, metal hydride storage has several advantages; metal hydride can store more hydrogen per unit volume and metal hydride storage is safer than pressure storage and cryogenic storage. To evolve hydrogen from the hydride, waste heat can be used. In addition, metal hydride absorbs and desorbs selectively hydrogen and thus hydrogen with high purity can be produced.

Magnesium has a high hydrogen storage capacity (7.6 wt%), is of low cost, and abundant in the earth’s crust. However, its reaction rate with H₂ is very low. A lot of work to improve the hydriding and dehydriding rates of magnesium has been performed by alloying magnesium with metals [1-3] such as Cu [4], Ni [5,6], and Ni and Y [7], by synthesizing compounds such as CeMg₁₂ [8] and MgₓTi₁₂Fe₁₂ₓNi₈ (x = 4, 8) [9], and by making composites such as Mg-20wt%Fe₂₃Y₈ [10]. Tanguy et al. [14] mixed metal additives with magnesium.

Reilly et al. [5] and Akiba et al. [6] improved the reaction kinetics of Mg with H₂ by preparing Mg-Ni alloys. Eisenberg et al. [15] plated nickel on the surface of magnesium to improve the hydriding-dehydriding kinetics of MgH₂. Song et al. [16-19] increased the hydriding and dehydriding rates of Mg by mechanical alloying of Mg with Ni under Ar atmosphere. Bobet et al. [20] improved the hydrogen-storage properties of both magnesium and Mg + 10 wt% Co, Ni, or Fe mixtures by mechanical grinding under H₂ (reactive mechanical grinding) for a short time (2 h). Aminorroaya et al. [11] added Nb and multi-walled carbon nanotubes to Mg-Ni alloys, and Cho et al. [12] added transition metals to cast Mg-Ni alloys for the improvement of the reaction rates of Mg with H₂. Milanese et al. [13] mixed Ni and Cu with Mg. We chose Ni as a transition element to be added.

Some works were performed by using magnesium hydride as a starting material in order to increase the hydriding and dehydriding rates of magnesium. Oelerich et al. [21], Dehouche et al. [22], and Barkhordarian et al. [23] increased the reaction rates of magnesium with hydrogen by planetary ball milling of magnesium hydride and metal, compound, or oxide.

Yavari et al. [24] developed nanostructured MgH₂ composites through the addition of transition metal fluorides such as FeF₃. A fluorine transfer reaction occurred to generate protective MgF₂ plus Fe nanoparticles as catalyst.
The powders showed sharply accelerated H-sorption kinetics at 573 K. They reported that H-sorption at rates acceptable for applications could be obtained at temperatures much lower than those reported for MgH2 with other catalysts without a significant loss of capacity.

The effect of transition metal fluorides on the dehydrogenation and hydrogenation of MgH2 has been investigated by Jin et al. [25]. Many of the fluorides showed a considerable catalytic effect on both the dehydrogenation temperature and hydrogenation kinetics of MgH2. Among them, NbF5 and TiF3 most significantly enhanced the hydrogenation kinetics of MgH2. They suggested that hydride phases formed by the reaction between MgH2 and these transition metal fluorides during milling and/or hydrogenation play a key role in improving the hydrogenation kinetics of MgH2.

Malka et al. [26] studied the influence of various halide additives milled with magnesium hydride (MgH2) on its decomposition temperature. The optimum amount of halide additive and milling conditions, the MgH2 decomposition temperature and energy of activation reduction, the difference in catalytic efficiency between chlorides and fluorides of the various metals were presented. They reported that the best catalysts, among the halides studied, for magnesium hydride decomposition were ZrF4, TaF5, NbF5, VCl3, and TiCl3.

The magnesium prepared by mechanical grinding under H2 (reactive mechanical grinding) with transition elements or oxides showed relatively high hydriding and dehydriding rates when the content of additives was approximately 20 wt%.

In this work, Ni and NbF5 were chosen as additives to enhance the hydriding and dehydriding rates of Mg. Samples with a composition of 80 wt% Mg-14 wt% Ni-6 wt% NbF5, which has the content of additives of 20 wt%, were prepared by reactive mechanical grinding. The hydriding and dehydriding properties of the material were subsequently examined. Here, 80 wt% Mg-14 wt% Ni-6 wt% NbF5 is denoted as Mg-14Ni-6NbF5.

2. EXPERIMENTAL PROCEDURES

Pure Mg powder (particle size 74-149 μm, purity 99.6%, Alfa Aesar), Ni (Nickel powder APS, 2.2-3.0 μm, purity 99.9 % metal basis, C typically < 0.1%, Alfa Aesar), and NbF5 (purity 98%, Aldrich) were used as starting materials.

Reactive mechanical grinding for the preparation of Mg-14Ni-6NbF5 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 (≈ 12 bar). The reactive mechanical grinding was performed for 6 h by repeating 15 min milling and 5 min rest. Hydrogen was refilled every two hour. A sample with a composition of Mg-10NbF5 was also prepared under the same conditions for the comparison of hydrogen properties of the samples with similar compositions.

The absorbed or desorbed hydrogen quantity was measured as a function of time by a volumetric method using a Sivert’s type hydriding and dehydriding apparatus described previously [27]. The quantity of the samples used to mea-