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Improvement in the hydrogen storage properties of Mg by mechanical grinding with Ni, Fe and V under H₂ atmosphere

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ABSTRACT

Mg-5wt%Ni-2.5wt%Fe-2.5wt%V (named Mg-5Ni-2.5Fe-2.5V) powder was prepared by reactive mechanical grinding using a planetary ball mill. The activation process, the changes in phase and microstructure with hydriding-dehydriding cycling, and the variations in the hydriding and dehydriding rates with temperature were investigated. The rate-controlling step for the dehydriding reaction of Mg-5Ni-2.5Fe-2.5V was analyzed by using a spherical moving boundary model. As the temperature increased from 473 K through 623 K, the initial hydrogen absorption rate under 12 bar H₂ decreased, while the hydrogen desorption rate under 1.0 bar H₂ increased.

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1. Introduction

Most of the research on the efficient hydrogen storage technologies has focused on the safe storage of hydrogen in high storage density and high capacity systems. Hydrogen can be stored using several methods such as storing hydrogen as a gas, liquid hydrogen storage, the physisorption of hydrogen, and storing it in the form of metal hydrides and complex hydrides, and via chemical reactions [1].

Magnesium, one of the promising hydrogen storage materials, has a high hydrogen storage capacity of about

7.6 wt% and is abundant in the earth's crust. However, its hydrogen absorption and desorption kinetics are very slow and occur at very high temperatures (at least 350–400 °C) and over a period of several hours.

The hydriding reaction of magnesium is hindered remarkably by several factors. One of them is the oxidation of the magnesium surface and/or formation of magnesium hydroxide [2]. The magnesium oxide layer, on the magnesium surface, prevents hydrogen molecules from penetrating into the material [3]. Therefore, a high-temperature activation process is needed to eliminate and/or crack the magnesium

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oxide layer [4,5]. Another factor is the limited dissociation rate of hydrogen molecules on the metal surface [6]. The pure magnesium surface is not active for the dissociation of the hydrogen molecules [7].

Song [8] reviewed the kinetic studies of the hydriding and dehydriding reactions of magnesium. The hydriding and dehydriding reactions of magnesium are nucleation-controlled under certain conditions and progress by a mechanism of nucleation and growth, and the hydriding rates of magnesium are controlled by the diffusion of hydrogen through the growing magnesium hydride layer. The hydriding and dehydriding kinetics of Mg can be improved, therefore, by a treatment such as mechanical alloying [9] which can facilitate nucleation by creating many defects on the surface and in the interior of Mg, or by the additive acting as active sites for the nucleation, and shorten diffusion distances by reducing the effective particle sizes of Mg.

Other studies reported different mechanisms; the growth of magnesium hydride is controlled by the slow migration of the interface between the hydride and magnesium [10,11], and by hydrogen diffusion along the hydride–metal interface rather than throughout the hydride layer [12].

Many studies have been conducted in an attempt to improve the reaction kinetics of magnesium with hydrogen by adding some catalytic materials and performing mechanical treatment and/or alloying [13]. The dissociation rate of hydrogen molecules, which indicates the degree of surface reactivity, can be improved by adding catalytic metals to reduce the activation energy. For example, elements Pd [14], Ni [15,16], Co, Ni or Fe [17,18], nanonickel [19], graphite [20,21], Ni and graphite [22], and V, Nb, Ti, and graphite [23] were added. Moreover, oxides and other compounds were added such as V, V₂O₅, VN, or VC [24], Cr₂O₃ [25], Nb₂O₅ [26–29], MgO [30], FeF₃ [31], organic additives [32,33], and Zr-based AB₂ hydride [34]. Nucleation can be facilitated by creating active nucleation sites and defects; these are made through mechanical treatment and/or alloying with additives [35]. The diffusion distance of hydrogen, which influences the growth rate of the magnesium hydride, can be decreased by mechanical treatment and/or alloying of Mg with additives, thereby reducing the magnesium particle sizes [2]. In addition, the hydrogen mobility can be improved by additives that create microscopic paths of hydrogen [2]. Consequently, a rough surface of magnesium possessing many cracks and defects is considered more advantageous for hydrogen absorption [36].

In this work, Ni, Fe, and V were selected as additives to improve the hydriding and dehydriding rates of magnesium. Ni is known to form Mg₂NiH₄, which has higher hydriding and dehydriding rates than magnesium. Fe is less expensive than Ni and may act as active sites for the dissociative chemisorption of H₂ [37]. V may also act as active sites for the dissociative chemisorption of H₂ like Fe. In our previous work, the addition of 10 wt% additive to Mg greatly improved the hydriding and dehydriding rates of Mg. The addition of Ni effectively improved the reaction rates of Mg with hydrogen, in particular the dehydriding rate of Mg mixtures. The weight percentage of the added Ni was thus 5, which was an important part of the additives, and another 5% consisted of Fe and V. The Mg-5wt%Ni-2.5wt%Fe-2.5wt%V powder, designated as

Mg-5Ni-2.5Fe-2.5V, was prepared by mechanical grinding under H₂ atmosphere (reactive mechanical grinding) using a planetary ball mill, which can lead to the formation of a powder with small particles, high surface reactivity and many inner defects. The hydrogen storage properties of this powder were then investigated.

2. Experimental procedures

The starting materials were pure Mg (particle size 75–150 μm, purity 99.6%), Ni (average particle size 2.2–3.0 μm, purity 99.9%), Fe (particle size <10 μm, purity 99.9%) and V (<45 μm, purity 99.5%) powders. Mg, Ni and Fe powders were provided by Alfa Aesar GmbH (Germany), and V powder was provided by Sigma–Aldrich (USA).

Reactive mechanical grinding was performed in two stages; Mg with Fe and V, and then with Mg and Ni. When Mg was milled with Ni, the interior of vial was coated with the Mg–Ni mixture, and homogeneous mixing was not possible. When Mg was milled with Fe and V, better mixing was achieved, and Mg and Ni were successfully added. Reactive mechanical grinding likewise in two stages led to a more homogeneous distribution of the additives in the alloy. The powders were mixed first to obtain the composition of Mg-5wt%Fe-5wt%V. The total weight of the mixture was 4 g, which was placed into a 250 ml stainless steel container with 105 hardened steel balls (total weight: 360 g), and the container was then hermetically sealed. All handling was performed in a glove box filled with Ar to prevent oxidation. Mechanical grinding using a planetary ball mill was performed at a disc revolution speed of 300 rpm under 12 bar H₂ for 1 h. Following this, the container was refilled to a pressure of 12 bar H₂, and mechanical grinding was performed for 1 h. The obtained mixture was then mixed with 4 g of Mg-10wt%Ni, resulting in the total powder weight of 8 g and the final composition of Mg-5wt%Ni-2.5wt%Fe-2.5wt%V. Reactive mechanical grinding was performed under the same conditions additionally for 13 h, refilling the hydrogen to a pressure of 12 bar H₂ every hour.

The hydrogen storage properties were measured as a function of time with a Sievert's type apparatus [38]. The powders were characterized by X-ray diffraction (XRD) using a Rigaku D/MAX 2500 powder diffractometer with Cu K α radiation. The microstructures of the powders were observed by a JSM-6400 scanning electron microscope (SEM) operated at 20 kV.

3. Results and discussion

After reactive mechanical grinding, MgH₂ was formed; however, Mg₂NiH₄, which was expected to be formed, was not detected. Ni and unreacted Mg were also found. Fig. 1 shows the XRD pattern of the dehydrided Mg-5Ni-2.5Fe-2.5V powder after 21 hydriding-dehydriding cycles. This sample contains Mg, Mg₂Ni, Fe, MgO, and Mg(OH)₂. Mg₂Ni is believed to have been formed during hydriding-dehydriding cycling, and Mg(OH)₂ is considered to have been formed by the reaction of Mg with water during treatment in air via the following reaction;

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