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Enhancement of hydrogen-storage properties of Mg by reactive mechanical grinding with oxide, metallic element(s), and hydride-forming element

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Abstract

In order to improve the hydrogen-storage properties of magnesium, oxides, metallic element(s) and a hydride-forming element were added to Mg by grinding under a hydrogen atmosphere (reactive mechanical grinding). As the oxides, Fe_2O_3 purchased, Fe_2O_3 prepared by spray conversion, MnO purchased, SiO_2 prepared by spray conversion, and Cr_2O_3 prepared by spray conversion were chosen. As the metallic elements, Ni, Fe, and Mo were selected. In addition, as the hydride-forming element, Ti was selected. Samples with the compositions of Mg–10 wt%oxide, 76.5 wt%Mg–23.5 wt%Ni, 71.5 wt%Mg–23.5 wt%Ni–5wt% Fe_2O_3, 71.5 wt%Mg–23.5 wt%Ni–5 wt%Fe, and Mg–14 wt%Ni–2 wt%Fe–2wt%Ti–2 wt%Mo were prepared. The hydrogen-storage properties and changes in phase and microstructure after the hydriding–dehydriding cycling of the prepared samples were then investigated.

Keywords: H_2-storage properties of Mg; Reactive mechanical grinding; Oxide; Metallic element; Hydride-forming element

1. Introduction

The development of efficient hydrogen storage technology is the main challenge in the forthcoming hydrogen economy, in which energy is stored and transported using hydrogen as an energy carrier for mobile applications (automobiles, aircraft, laptops, etc.). Most of the research on this topic has focused on storing hydrogen safely in lightweight, compact and high capacity systems. There are several hydrogen storage methods currently being investigated: 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 is considered as one of the prospective hydrogen storage materials. It 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 rates are very low and its hydrogen absorption and desorption occur at quite high temperatures (at 350–400 °C and over a period of several hours).

Song [2] reviewed the kinetic studies of the hydriding and dehydriding reactions of Mg. Many works do not agree with one another on the rate-controlling step(s) for hydriding or dehydriding reactions of magnesium. However, it is generally accepted that the hydriding and dehydriding reactions of Mg are nucleation-controlled under certain conditions and progress by a mechanism of nucleation and growth, and that the hydriding rates of Mg are controlled by the diffusion of hydrogen through a growing Mg–hydride layer. The hydriding and dehydriding kinetics of Mg can be improved, therefore, by a treatment such as mechanical alloying, which can create defects on the surface and/or in the interior of Mg and reduce the particle sizes of Mg.

The oxides are brittle and, thus, they may be pulverized during mechanical grinding. The added oxides and/or their

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pulverization during mechanical grinding may help the particles of magnesium become finer. Oelerich et al. [3] produced nanocrystalline MgH_2 with the addition of V_2O_5, VN, VC, or high-purity V by high-energy ball milling. The results showed a significant enhancement of the hydrogen reaction kinetics under the chosen experimental conditions only for V_2O_5, VN, and VC, while the influence of high-purity V was negligible. Dehouche et al. [4] investigated the long-term cycling stability as well as the thermal stability of the hydriding–dehydriding properties of nanostructured MgH_2 with 0.2 mol% Cr_2O_3 catalyst addition synthesized by ball milling. High hydriding rates were maintained for at least 17 cycles at 623 K and at least 1000 cycles at 573 K. Barkhordarian et al. [5,6] reported that Nb_2O_5 was superior to all other previously investigated catalysts for the hydrogen sorption reaction of magnesium. They attributed the catalytic effect to electronic exchange reactions with hydrogen molecules, accelerating the gas–solid reaction. Friedrichs et al. [7] and Friedrichs et al. [8] improved the hydrogen sorption kinetics of MgH_2 by milling MgH_2 mechanically with Nb_2O_5 nanoparticles (15 nm). Working as catalysts of reaction products from the Mg–Nb_2O_5 during cycling, and generating gateways of reaction products from the reduction of Nb_2O_5 for further hydrogen diffusion were proposed as two possible reasons for the improvement of the hydrogen sorption kinetics of Mg by them [7]. Aguey-Zinsou et al. [9] improved the (de)hydriding properties of magnesium significantly by mechanical milling MgH_2 with MgO. The MgH_2 particles had an average nanometric size of 0.44 ± 0.3 μm. They reported that the addition of MgO to the grinding medium, which has good lubricant and dispersing properties, allowed the particle size of MgH_2 to be further decreased by reducing the agglomeration and cold welding.

Huot et al. [10] showed that the rapid synthesis of the metal hydride could be achieved by milling at elevated temperature under hydrogen pressure by adding V and graphite to Mg. Liang et al. [11] prepared MgH_2–Tm (Tm = 3d-transition elements Ti, V, Mn, Fe, Ni) nanocomposite powders by intensive mechanical milling. Desorption was most rapid for MgH_2–V, followed by MgH_2–Ti, MgH_2–Fe, MgH_2–Ni and MgH_2–Mn at low temperatures. The composites containing Ti exhibited the most rapid absorption kinetics, followed in order by Mg–V, Mg–Fe, Mg–Mn and Mg–Ni. Li et al. [12] prepared Mg–20 wt% Ni–Y composite by reactive mechanical alloying (RMA). The composite exhibited excellent hydrogen sorption kinetics and did not need activation in the first hydrogen storage process.

Bobet et al. [13] reported that mechanical alloying in H_2 (Reactive Mechanical Grinding) for a short time (2 h) is an effective way to improve the hydrogen-storage properties of both magnesium and Mg + 10 wt% Co, Ni or Fe mixtures. Palade et al. [14] prepared magnesium-rich Mg–Ni–Fe intermetallic compounds and reported that the short time ball milling of the ribbons obtained by melt spinning displayed a better hydrogen desorption kinetics than the long time ball milling of a mixture of MgH_2, Ni and Fe powders. The former preserved a better hydrogen desorption kinetics than the latter.

In this work, in order to enhance the hydrogen-storage properties of magnesium, Mg–oxide and Mg–oxide-metallic element(s) hydrogen storage alloys were prepared by grinding under a hydrogen atmosphere. The hydrogen storage properties and changes in phase and microstructure after hydriding–dehydriding cycling were then investigated.

2. Experimental details

Mg (particle size 297–100 μm, purity 99%, Fluka), Fe_2O_3 (<5 μm, purity 99+%, Aldrich), Fe_2O_3 (36 nm, prepared by spray conversion), Cr_2O_3 (18 nm, prepared by spray conversion), MnO (88–250 μm, purity 99%, Aldrich), SiO_2 (99 nm, prepared by spray conversion), Ni (~5 μm average, purity 99.9%, CERAC), Fe(<5 μm, purity 99+, Aldrich), Ti (−325 mesh, purity 99.98%, Aldrich), and Mo (1–2 μm, purity 99.9%, Aldrich) were used as starting materials. The preparation of the oxides by spray conversion is explained in detail in reference [15]. A mixture with the desired composition (total weight = 8 g) was introduced into 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 mill container with a volume of 250 ml was then filled with high purity hydrogen gas at a pressure of about 10 bar. The reactive mechanical grinding was performed with a disc revolution speed of 250 rpm.

The quantity of absorbed or desorbed hydrogen was measured as a function of time using a volumetric method. A Sievert's type hydriding and dehydriding apparatus comprised of stainless steel pipes is described in Ref. [16]. The hydrogen pressure was maintained at a nearly constant level during the hydriding and dehydriding reactions by dosing or removing an appropriate quantity of hydrogen from or into a standard volume. The variation of the hydrogen pressure in the standard volume portion allows one to calculate the quantity of hydrogen absorbed or desorbed by the sample as a function of time.

Rietveld analysis of the X-ray diffraction (XRD) patterns was carried out using the FullProf program for the dehydrided sample after activation. The microstructures were observed by Scanning Electron Microscope (SEM).

3. Results and discussion

Samples with the compositions Mg–10 wt% oxide (oxide = Fe_2O_3 purchased, Fe_2O_3 prepared by spray conversion, MnO purchased, SiO_2 prepared by spray conversion, and Cr_2O_3 prepared by spray conversion) were prepared by milling for 2 h under high purity hydrogen at a pressure of about 10 bar. We refer to Mg–10 wt%oxide as Mg–10oxide. Fig. 1 shows the weight percentage of absorbed hydrogen, H_a, versus t curves after activation obtained at 593 K and 12 bar H_2 for these samples. The weight percentage of absorbed hydrogen, H_a, is expressed with respect to the sample weight. Mg–10Cr_2O_3 prepared by spray conversion has the highest hydriding rate, followed in order by the Mg–10oxide samples with oxide =