Hydrogen Storage Property Comparison of Pure Mg and Iron (III) Oxide-Added Mg Prepared by Reactive Mechanical Grinding

Myoung Youp Song1,*, Sung Nam Kwon2, and Hye Ryoung Park3

1Division of Advanced Materials Engineering, Hydrogen & Fuel Cell Research Center, Engineering Research Institute, Chonbuk National University, 567 Baekje-daero Deokjin-gu Jeonju 561-756, Korea
2Department of Hydrogen and Fuel Cells, Graduate School, Chonbuk National University, 567 Baekje-daero Deokjin-gu Jeonju 561-756, Korea
3School of Applied Chemical Engineering, Chonnam National University, 300 Yongbong-dong Buk-gu Gwangju 500-757, Korea

Abstract: The activation of Mg-10 wt%Fe2O3 was completed after one hydriding-dehydriding cycle. Activated Mg-10 wt%Fe2O3 absorbed 5.54 wt% H for 60 min at 593 K under 12 bar H2, and desorbed 1.04 wt% H for 60 min at 593 K under 1.0 bar H2. The effect of the reactive grinding on the hydriding and dehydriding rates of Mg was weak. The reactive grinding of Mg with Fe2O3 is believed to increase the H2-sorption rates by facilitating nucleation (by creating defects on the surface of the Mg particles and by the additive), by making cracks on the surface of Mg particles and reducing the particle size of Mg and thus by shortening the diffusion distances of hydrogen atoms. The added Fe2O3 and the Fe2O3 pulverized during mechanical grinding are considered to help the particles of magnesium become finer. Hydriding-dehydriding cycling is also considered to increase the H2-sorption rates of Mg by creating defects and cracks and by reducing the particle size of Mg.

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1. INTRODUCTION

Metal hydride storage can store more hydrogen per unit volume and is safer than pressure storage and cryogenic storage. Waste heat can be used for the release of hydrogen from the hydride. Moreover, metal hydride absorbs and desorbs selectively hydrogen and thus hydrogen with high purity can be produced [1].

Magnesium has many advantages for a hydrogen storage material such as large hydrogen storage capacity (7.6 wt%), low cost and abundance in the earth’s crust. In spite of these advantages, its hydriding and dehydriding kinetics are very slow [2]. A lot of work to ameliorate the reaction kinetics of magnesium with hydrogen has been done by alloying certain metals with magnesium [3-11], mixing metal additives with magnesium [12], or plating nickel on the surface of magnesium [13].

Song [14] reviewed the kinetic studies of the hydriding and the dehydriding reactions of Mg. Many works do not agree with one another on the rate-controlling step(s) for hydriding or dehydriding of magnesium. However, there is no refutation in the points 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 [15-17] which can create many defects on the surface and in the interior of Mg, and reduce the particle size of Mg.

The oxides are brittle, and thus they may be pulverized during mechanical grinding. The added oxides and the oxides pulverized during mechanical grinding may help the particles of magnesium become finer.

In this work, pure Mg was ground under H2, and a Mg
10 wt%Fe$_2$O$_3$ sample was prepared by mechanical grinding under hydrogen (reactive mechanical grinding) in a planetary ball mill, and their hydrogen-storage properties were investigated and compared.

2. EXPERIMENTAL DETAIL

Starting materials were pure Mg (Fluka, particle size about 300–106 μm, purity ≥ 99%), and iron (III) oxide (nano-sized Fe$_2$O$_3$, prepared by spray conversion process, about 36 nm) [18,19]. The purity of used H$_2$ was 99.999%. Pure Mg powder was mixed with 10 wt% Fe$_2$O$_3$ (total weight = 8 g) in a stainless steel container (with 105 hardened steel balls, total weight = 360 g) closed in a hermetic way. All the handlings were performed in a glove box under Ar in order to prevent oxidation. The mill container was then filled with high purity hydrogen gas (12 bar). The disc revolution speed was 250 rpm, and 15 min milling and 5 min rest were repeated eight times, resulting in the total milling time of 2 h. There reactive mechanical grinding conditions (sample to ball weight ratio, disc revolution speed, and milling time) were the optimum ones for preparation of Mg-10 wt%Fe$_2$O$_3$ from the purchased Fe$_2$O$_3$ [20]. Pure Mg was also ground under the same conditions.

The employed Sievert’s type volumetric high-pressure hydriding and dehydriding apparatus was described previously [21]. The absorbed or desorbed hydrogen quantity was measured as a function of time by a volumetric method. The used sample weight was 1.0 g. The microstructures were observed by scanning electron microscope (JSM-6400 Scanning Electron Microscope) at 20 kV.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows microstructures of pure Mg after reactive mechanical grinding. After reactive mechanical grinding, particles of pure Mg become larger than those of purchased pure Mg (particle size; 300–106 μm), and have fine cracks on the surfaces of Mg particles. Ductile Mg powders formed plastically into elongated shape by collisions between balls and fine cracks formed by repeated impact forces during ball milling. However, growth rate of micro-cracks were very slow and fine power could not obtained by milling for 2 hours.

Microstructures of Mg-10 wt%Fe$_2$O$_3$ after reactive mechanical grinding are exhibited in Fig. 2. Particles of this sample are smaller than those of pure Mg. Some particles are not ground, and fine particles are agglomerated. Fe$_2$O$_3$ volume percentage in Mg-10 wt% Fe$_2$O$_3$ calculated from densities (Mg: 1.74 g/cm$^3$, Fe$_2$O$_3$: 5.24 g/cm$^3$) and weight percentage of each phase is 3.56 vol.%. Nano-sized oxide (3.56 vol.%) can be distributed uniformly on Mg particles and diminish coagulations of ductile Mg particles or Mg adhering on balls and milling container walls. So, more Mg fine power can be formed during ball milling.

The percentage of absorbed hydrogen H$_a$ is expressed with respect to the sample weight. The variation of absorbed hydrogen quantity (H$_a$) versus time curve with the number of cycles (n) at 593 K under 12 bar H$_2$ for pure Mg was examined. A hydriding-dehydriding cycle consisted of hydriding at 593 K under 12 bar H$_2$ for 1 h and dehydriding in vacuum for 2 h. As the number of cycles increased, the hydriding rate decreased. It is believed because particles became sintered and the