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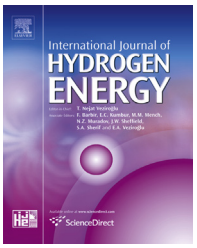

Hydrogen storage properties and mechanisms of magnesium based alloys with mesoporous surface

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ABSTRACT

A new kind of magnesium based hydrogen storage alloy with highly developed surface (HDS) was prepared using the technique of mechanical alloying followed by alkali washing in this paper. The phase composition, morphology, hydrogen storage properties and mechanisms of the alloy thus prepared, named HDS Mg-Ni, were further investigated by multiple methods including X-ray diffraction, scanning electron microscope, Sieverts volumetric method and differential scanning calorimeter. The specific surface area, average pore size and pore volume of the alloy are 50.95 $m^2\ g^{-1}$, 36.2 nm and 0.34 cc g^{-1}, respectively. Also, it was discovered that the HDS Mg-Ni powder takes in about 0.65 wt.% of hydrogen even at a low temperature of 323 K, at which the conventional Mg and Mg_2Ni materials could not react with H_2. It suggests that the highly developed surface remarkably improves the hydrogen storage properties at low temperatures. Besides, the synergistic effects between the HDS Mg-Ni powder and activated carbon(AC) on the improvement of low-temperature behaviors were discussed. The results showed that the addition of AC further improves the hydrogen capacity and absorption kinetics due to the increased specific surface area, providing easier and more paths for the diffusion of hydrogen into the alloy powder.

Introduction

As is well known, hydrogen energy is viewed as a kind of ideal alternative energy because of its non-pollution and cyclic utilization. In order to achieve the practical application of hydrogen energy, the efficient, safe and economic hydrogen storage is a must, since the application process has the dispersibility and discontinuity [1]. Among all the hydrogen storage means, the solid state hydrogen storage is regarded as the promising practicable technology because of its high energy density, good security and excellent rechargeable characteristics [2–4]. In view of high hydrogen content, low price and friendly to environment, Mg and Mg-based alloys have been increasingly investigated [5]. Nevertheless, the practical application of Mg and Mg-based alloys is hindered by their high stability, which results in bad kinetics and high reaction temperature [6].

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A breakthrough in improving the hydrogen absorption/desorption kinetic properties of Mg and Mg-based alloys was achieved by using mechanical alloying (MA) as the preparation method [7–9]. The process of MA continuously refines the micro-structure and generates lots of defects and micro-strains in the crystal lattice, which are beneficial to the diffusion of hydrogen into the unreacted layer and the destabilization of the alloys. Bardhan et al. [10] and Cheng et al. [11] held the opinion that small particle sizes, large surface area and abundant defects are beneficial for obtaining Mg-based alloys with fast sorption kinetics. Denys et al. [12] prepared Mg-based metal alloys with sizes below 10 nm and discovered that particle refinement could facilitate rapid hydrogen absorption/desorption processes.

Since a remarkable improvement on hydrogen absorption/desorption kinetic properties of Mg-based alloys has been achieved, more and more researchers and institutions around the world focus on the improvement of the thermodynamic behaviors of Mg and Mg-based alloys, especially on the reduction of the hydrogen absorption/desorption temperatures. Many approaches have been attempted to improve the thermodynamics and reduce the reaction temperature. The two approaches, mixing catalysts or other hydrogen storage materials [13–17] and modifying the microstructure [18–22], are widely used to improve the thermodynamics of Mg and Mg-based alloys. Yao et al. [13] systematically analyzed the effects of carbon nanotubes and metallic catalysts on hydrogen absorption/desorption properties of magnesium nanocomposites. It was discovered that mixing carbon nanotubes reduces the starting temperature of the desorption reaction of MgH_2 by 60 K. Agarwal et al. [16] reduced the hydrogen desorption temperature of MgH_2 down to 523 K using the additive of 25 wt.% of ZrCrCo alloy. On the other hand, the approach of the microstructure modification to improve the thermodynamics of Mg and Mg-based alloys has been increasingly investigated nowadays, since the stability is greatly associated with the microstructure. A kind of porous Ni layer microencapsulated Mg, namely porous Ni@Mg, was successfully synthesized through the reduction reaction of Ni^{2+} by Mg in $NiCl_2.12H_2O$ solution by Chai et al. [18]. It was discovered that Ni@Mg takes up about 0.38 wt.% of hydrogen at 373 K under the pressure of 5 MPa, while temperature higher than 573 K is required for pure Mg to absorb hydrogen. Although the hydrogen absorption/desorption thermodynamic properties of Mg-based alloys have been improved by some degree according to the abovementioned researches, the reaction temperature for hydrogen storage is still too high for practical applications. Therefore, there is significance and great value in looking for other methods to further improve the thermodynamic behaviors of Mg-based hydrogen storage alloys.

In the present study, the powders of Mg, Ni and Al were used as the starting materials to first synthesize the Mg-Ni-Al powder by mechanical alloying, then alkali washing method was applied to remove Al for preparing the Mg-based alloy with highly developed surface. Subsequently, the phase composition, micro-morphology of the as-prepared Mg-based alloy mixed with and without activated carbon (AC), labeled respectively as HDS Mg-Ni and composite Mg-Ni-AC, were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM) measurements. The specific surface area, average pore size and pore volume of the two samples were examined by applying Brunauer–Emmertt–Teller (BET) measurement. Sieverts volumetric method and differential scanning calorimeter (DSC) experiments were carried out to measure the kinetics and thermodynamics of the hydrogen absorption/desorption processes, respectively. Besides, the hydrogen storage mechanisms of this kind of Mg-based alloy with mesoporous surface were also discussed in detail.

Experimental

Sample preparation

Elemental powders of Mg (200 mesh, 99% purity), Ni (200 mesh, 99.5% purity) and Al (200 mesh, 99.99% purity) with a mole ratio of 2:1:3 were ball-milled in the argon atmosphere to synthesize the Mg-Ni-Al alloy as pre-synthesis. About 8 g of a mixture of Mg (8 wt.% excess to protect Ni powder from oxidation), Ni and Al powders was loaded into a sealed tungsten carbide tank with ten tungsten carbide balls of 10 mm diameter in a glove box filled with pure argon. During MA, benzene was used as the process control agent to prevent the mixed powders from agglomerating and adhering to the walls. The ball-to-powder weight ratio was set to be 10:1. Then, the sealed tungsten carbide tank with the mixed powder was put into a planetary ball mill (Retsch PM100) and processed for 70 h in the speed range from 350 to 450 rpm, thereby synthesizing the Mg-Ni-Al alloy. Thereafter, the Mg-Ni-Al alloy was further treated with strong alkaline solution of NaOH (20 wt.%) at the temperature of 343 K with ultrasonic wave to remove aluminum from the alloy. Subsequently, the treated sample was rinsed for several times by distilled water till the pH value of filtrate was 7, meaning that the strong alkaline solution was completely washed off. The alkali washing process generated many vacancies at the positions of removed aluminum. These vacancies on the surface of the alloy resulted in the HDS Mg-Ni sample having many pores in its structure. It should be noted that the whole treatment process must be operated in protective gas atmosphere to avoid oxidation of the samples. The HDS Mg-Ni sample was then divided into two groups, one of which was further mixed with AC by a mole ratio of 2:1 and ball milled for 14 h under the protection of argon, resulting in the synthesis of the composite Mg-Ni-AC powder.

Sample characterization

The phase composition of the prepared HDS Mg-Ni and composite Mg-Ni-AC powder were determined by XRD analysis, which was performed in the 2θ range from 15° to 80° with a rate of $6^\circ \cdot min^{-1}$ at room temperature using X'pert Pro (PANalytical, Cu $K_\alpha/\lambda = 0.15405$ nm, 40 kV, 300 mA). BET measurement was carried out on Auto-sorb-1 (Quantachrome Corporation) by nitrogen-argon adsorption at 77 K with an N_2/Ar ratio of 30/70 for getting the specific surface area, average pore size and pore volume of the samples. Besides, a JEOL JSM-6390A SEM instrument was applied to make morphology identification of the samples.

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