Hydrogen storage properties of Mg-23.3wt.%Ni eutectic alloy prepared via hydriding combustion synthesis followed by mechanical milling

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ABSTRACT:

A Mg-23.3wt.%Ni eutectic alloy was prepared by the process of hydriding combustion synthesis followed by mechanical milling (HCS+MM). The product showed a high hydriding rate at 373 K and the dehydrogenation started at temperature as low as 423 K. Several reasons contributing to the improvement in hydrogen storage properties were presented. The result of this study will provide attractive information for mobile applications of magnesium hydrogen storage materials, and the process of HCS+MM developed in this study showed its potential for synthesizing magnesium based hydrogen storage materials with novel hydriding/dehydriding properties.

KEYWORDS: Hydrogen storage materials; magnesium alloys; mechanical milling; hydriding combustion synthesis.

Introduction

Hydrogen has been praised as a clean energy with great potential. It can be converted into electricity using a proton exchange membrane fuel cell (PEMFC), which will power road vehicles in near future. Among many challenges for industrialization of this technique is to develop an effective system for hydrogen storage. For a practically applicable hydrogen storage system for mobile applications, the operating requirements include these criteria: appropriate thermodynamics, fast kinetics for hydrogen uptake and release, high storage capacity and long lifetime for absorption and desorption. Currently, hydrogen can be stored in three different forms: compressed gas, cryogenic liquid and solid. Solid-state hydrogen storage has been considered as the most attractive method. It refers to storage of hydrogen though reversible reactions between hydrogen and a chemical compound, such as intermetallics [1], metal complex [2] and nitrides [3], or though physisorption by materials with high surface area, such as carbon nanotubes [4-6], metal-organic frameworks [7] and zeolite [8]. Unfortunately, no existing hydrogen materials or systems can meet all those aforementioned criteria for mobile applications in the present.

Magnesium and its alloys are powerful candidates for mobile hydrogen storage, due to their high specific hydrogen capacity, abundance in resources and low environmental impact. Up to now, numerous investigations have been initiated aiming to overcome their poor hydrogen sorption and desorption kinetics as well as high operating temperature. One of the most widely used method applied for preparing magnesium based hydrogen storage materials is mechanical milling, a well-known non-equilibrium solid state processing method for synthesizing nano-grained alloys, amorphous alloys, super saturated solid solutions and intermetallic compounds[9]. Remarkable improvements in hydriding and dehydriding kinetics have been achieved by mechanical milling of magnesium with a variety of additives, such as element metals [10, 11], oxides [12] and intermetallics [13,14].

Besides mechanical milling, hydriding combustion synthesis has been regarded as an innovative method for preparation of magnesium-based hydrogen storage materials, offering several merits, such as short processing time and high product activity. This method was first applied to synthesis Mg2Ni hydride directly from mixture of metal powders in a hydrogen atmosphere, and was later used to synthesis systems like Mg-x%Ni(x=1~55) [15], Mg-X(X=Fe, Co)[16], Mg-Ni-X(X=Cu, Ag) [17-18], and La-Mg-Ni [19]. Very recently, in an exploration to investigate the effect of mechanical grinding on the hydriding and dehydriding behaviors of Mg2Ni alloy synthesized by hydriding combustion synthesis, we found that the as-milled product absorbed
hydrogen at 313 K with a surprisingly high rate and the desorption commenced at a temperature as low as 370 K [19].

In order to gain a higher hydrogen capacity at temperature low than 373 K, here we mechanical alloyed the hydride of Mg-Ni eutectic system (atomic ratio: Mg/Ni=7.85, the theoretical hydrogen capacity is 5.9wt.%) prepared by hydriding combustion synthesis. The hydriding and dehydriding properties of the product are presented and discussed in the paper.

Experiment
For hydriding combustion synthesis, we use commercially available magnesium (less than 78mm in diameter and 99% in purity) and nickel (2~3mm in diameter and 99.9% in purity) powders. Some details of the pretreatment method of the powder mixtures and the synthesis conditions of hydriding combustion synthesis were the same as that described in Ref. [20]. A planetary milling equipment with stainless steel vials of 50 cc was employed for mechanical milling. The as-synthesized product was used directly without any crashing treatment for mechanical milling in argon atmosphere at 200rpm of rotate speed and 30:1 of ball to powder ratio. Small amount of graphite (5wt.%) was added into the milling vial as a lubricant to avoid excessive sticking of powders to the milling balls and the wall of the milling vial.

As both the product of hydriding combustion synthesis (hereinafter referred as HCS) and the product of hydriding combustion synthesis followed by mechanical milling (hereinafter referred as HCS+MM) were hydrides, measurement of hydriding rates at different temperatures (in the order of 313 K, 343 K and 373 K) were taken prior to a dehydriding process at 523 K in vacuum for 60 min. Pressure-composition-isotherms (PCT) at temperatures of 473 K and 523 K were measured afterwards. The amount of the specimen used for the hydriding test was around 0.5 gram. The dehydriding property was measured by heating the specimen in the evacuated sample chamber at a heating rate of 20 K/min. Tran [21] used a similar technique to determine the temperatures at which the hydriding and dehydriding reaction take place. The temperature and the pressure change were regularly recorded; thereby the amount of hydrogen desorbed as a function of temperature can be derived. All handlings of the product of HCS+MM were carried out in a glove box filled with argon so as to minimize oxidation of the sample.

Results and discussion
Figure 1 shows the hydriding rates at temperatures of 313 K, 343 K and 373 K. The HCS+MM product absorbed hydrogen at a very high rate. It reached the saturated hydrogen capacity of 4.15wt.% within less than 100 sec at 373 K, while the HCS product only absorbed 2.10wt.% in 800 sec at 373 K. At the temperature of 313 K, it can be also clearly seen that the hydriding rate of the HCS+MM product is far large than that of the HCS product, which only absorbed 0.16wt.% of hydrogen.
The marked increase in hydriding rates by mechanical milling of the HCS product can be understood by considering the following factors. First, the mechanical process generally involves repeated fracture and cold welding, which not only result in pulverization of the particles as well as refinement of grains contributing to a decrease in diffusion length for hydrogen uptake, but also introduce a great amount of various defects to the HCS product that may serve active sites for hydrogenation. Second, milling of hydrides is advantageous comparing to milling of metals and intermetallics [22], because the brittle nature of metal hydrides will lead to an easier mechanical pulverization process. Last, the high activity of the HCS product may of course contribute, to a great extent, to the high activity as well as the fast hydriding kinetics.

The plot of the amount of hydrogen desorbed as a function of temperature is shown in Fig. 2. The dehydriding curve of the HCS product (hollow marks) and the HCS+MM product (filled marks) were obtained by heating the as-synthesized specimen in evacuated sample chamber. The amount of hydrogen stored in the HCS product were 4.2wt.% (this value was reached at 645 K and did not increase further in higher temperatures). Theoretically, the hydrogen content for Mg-Ni eutectic (Mg/Ni=7.85) system is 5.9wt.%, which is 1.7wt.% higher than that we obtained in Fig. 2. This offset in hydrogen capacity can be clarified by the XRD result, which reveals that the HCS product was not fully hydrogenated, containing unreacted magnesium and the solid solution phase Mg2NiH0.3.

As evidenced in Fig. 2 the dehydriding onset (the temperature at which the dehydrogenation reaction begins) decreased drastically from around 560 K of the HCS product to 423 K of the HCS+MM product. This result implied that the hydride of Mg-Ni eutectic alloy prepared by HCS was destabilized by the mechanical process, which agrees well with the DSC trace of the mechanically grinded Mg2NiH4 or mixture of Mg2NiH4 and MgH2 reported by Zulaski [23], who concluded that the mechanical process led to a decrease in activation energy for dehydrogenation, but not changing the thermodynamic property. Furthermore, the oxide layer resided in the alloy surface must have been substantially destructed by mechanical milling, and carbon, which was used as a lubricant in this study, were found to prevent the restoration of the oxide layer in hydriding/dehydriding cycles due to its strong reducing character [24, 25]. As a result, the diffusion of hydrogen atoms during dehydriding could be accelerated and the dehydriding property was improved.

Figure 3 shows the pressure-composition-isotherms (PCIs) of the HCS+MM product. It can be seen that the PCIs of absorption has two plateaus, of which the lower plateau belong to magnesium and the higher belong to Mg2Ni. A large hysteresis was observed in both temperatures of 473 K and 523 K, such that the equilibrium pressures of desorption were much lower than that of absorption. The product does not desorb hydrogen at 473 K within the testing pressure range of 0.01 MPa~1.2MPa, implying that mechanical milling may not destabilized the hydride thermodynamically and change the decompose enthalpy substantially.

From the hydriding result shown in Fig. 1 as well as the PCIs shown in Fig. 3, The hydrogen capacity of the HCS+MM product did not reach the theoretical value of 5.9wt.%. This can be ascribed to oxidation during the process HCS, MM and most importantly, during handlings of the specimen in the glove box that may contain un-removed oxygen. Actually, the HCS+MM product exhibited strong affinity for oxygen, such that it caught fire immediately after exposed to air.
Conclusions
The Mg-Ni alloy with a eutectic composition was prepared by hydriding combustion synthesis followed by mechanical milling (HCS+MM). The saturated hydrogen capacity of 4.2wt.% was reached within only 100 sec at 373 K and the dehydrogenation reaction began at a temperature as low as 423 K. This result is very attractive for application of magnesium alloys for mobile hydrogen storage, and the process of HCS+MM developed in this study showed its potential for synthesizing magnesium based hydrogen storage materials with novel hydriding/dehydriding properties.

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Reference


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