Effect of surface oxidation on the hydriding and dehydriding of Mg$_2$Ni alloy produced by hydriding combustion synthesis

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Abstract Hydriding combustion synthesis (HCS) has been regarded as an innovative process for the preparation of high active magnesium-based hydrogen storage alloys. For the purpose of understanding the interrelation of the unique hydrogen storage properties and the surface characteristics of the HCS product, the samples of Mg$_2$Ni alloy/hydride with and without exposure to air were prepared from the HCS product of Mg$_2$NiH$_4$. The hydriding and dehydriding properties were compared and the surface compositions were analyzed by means of X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES). It was shown that the air exposure considerably decreases the hydriding activity of Mg$_2$Ni. Absorbing of 3.0 wt.% of hydrogen under the conditions of 603 K and 3.0 MPa after the air exposure takes 1500 s, which is six times longer than for the unexposed alloy. The hydrogen desorption of the hydride are also impeded by the air-exposure, which results in the increase of dehydriding temperature from 450 K to 540 K. XPS and AES analyses indicated that Mg segregates and exists in the form of hydroxide on the surface of the air-exposed sample, which is responsible for the degradation of the hydriding and dehydriding properties. It was confirmed that the fresh surfaces generated during the dehydriding process of the as-synthesized hydride product contributes to the high activity of the HCS product in the first cycle of the hydriding determination.

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Introduction

It is well known that the storage medium is very important for the practical use of hydrogen energy. Compared with the other methods of hydrogen storage, the reversible metal hydrides are most effective and safe. Among the developed hydrogen storage alloys, magnesium-based alloys are potentially promising due to their high hydrogen capacity, low specific weight, abundant raw materials and low environment impact. However, its poor hydriding–dehydriding kinetics and high operation temperature become the main obstacles encountered with the applications. Up to now, many investigations have been carried out to overcome these disadvantages by utilization of new preparation methods. For example, the hydriding and dehydriding properties of magnesium-based hydrogen storage alloys can be notably improved by mechanical alloying (MA) or ball milling due to the reduction of grain size, the generation of large numbers of defects and the catalysis of second dispersed phase [1–4].

Recently, another preparation method called hydriding combustion synthesis (HCS) has been regarded as an innovative process to produce magnesium-based hydrogen storage alloys [5–7]. By means of HCS, a porous magnesium-based hydride can be obtained directly by only one step combining the synthesis and the hydrogenation of the alloy. In addition, the synthesis temperature of HCS is lower than 873 K. So the evaporation of magnesium can be limited effectively and the addition of excess magnesium is not required, which is always necessary in the conventional

melting process of ingot metallurgy (IM). The remarkable advantages of the HCS are short process time, low energy requirement and high purity of the product [8–10]. More attractively, the HCS product of Mg_2NiH_4 possesses excellent hydriding activity. It absorbs saturated content of hydrogen quickly in the first hydriding process without any activation treatment [11].

In our previous work, we reported that the composition of the outmost surface layer of the as-synthesized HCS product of Mg_2NiH_4 was $Mg(OH)_2$ instead of MgO, and that the fresh surface was generated during the first dehydriding process, these were beneficial for the hydriding activity of the HCS product [12]. However, there have been no detailed studies on the surface characteristics of the as-dehydrogenated product of HCS prior to the first hydrogen uptake, and the relationship between surface oxidation and hydrogen storage properties of the HCS product is still unclear. Therefore, in this paper, samples corresponding to different hydrogenation–dehydrogenation stages and air-exposed states of the HCS product were prepared, and then the surface characteristics of the as-dehydrogenated product of HCS, as well as the effect of surface oxidation on the hydriding–dehydriding properties of the HCS product were studied systematically.

Experimental details

Sample preparation

The HCS product was prepared from commercially available magnesium and nickel powders. The magnesium powder is 99.9 mass% in purity and <177 μm in particle size and the nickel powder is 99.7 mass% in purity and 2–3 μm in size. They were well mixed in 2:1 of Mg:Ni molar ratio by an ultrasonic homogenizer in acetone for 1 h. After completely drying in air, the well-mixed powder was placed directly into the synthesis reactor without any compressive treatment. Then it was heated to 850 K at the rate of 7 K/min and held for 1 h in hydrogen atmosphere with the initial pressure of 1.8 MPa. The synthesis reactor used in this study is the same as reported in [12].

Five samples were prepared in this study. Sample 1 was the as-synthesized HCS product with a particle size distribution of 75–150 μm. X-ray diffraction (XRD) and Rietveld analysis indicated that sample 1 was composed of 83.4 wt.% Mg_2NiH_4 and 16.6 wt.% $Mg_2NiH_{0.3}$. Sample 2 was the as-dehydrogenated product of sample 1 and never exposed to air, and sample 3 was obtained by exposing sample 2 to air for about 5 min. The XRD indicated that the phase compositions of samples 2 and 3 were both the pure Mg_2Ni. Sample 4 was the first fully hydrogenated product of sample 2 and never exposed to air, and sample 5 was obtained by exposing sample 4 to air for about 5 min. The phase compositions of samples 4 and 5 were both the pure Mg_2NiH_4. Table 1 summarizes the characterization and phase composition of the samples. Here, samples 2 and 3 were arranged to investigate the effect of surface oxidation on the hydriding property of Mg_2Ni, and samples 1, 4 and 5 were arranged for comparing the dehydriding property of Mg_2Ni hydride before and after surface oxidation.

Sample characterization

The hydrogenation–dehydrogenation treatment and the determination of hydriding–dehydriding properties of samples were performed using a Gas Reaction Controller. For the measurement of hydriding property, the sample was heated to the temperature of 603 K or 553 K in vacuum firstly, and then hydrogen with the pressure of 3.0 MPa or 1.5 MPa was introduced into the sample chamber. The amount of hydrogen absorbed as a function of time was obtained based on the conventional isovolumetric method. The dehydriding property was determined by heating the sample in vacuum to 603 K at the rate of 20 K/min. The pressure of hydrogen desorbed and the temperature were recorded automatically at a regular interval of 6 s by a computer. Then the amount of hydrogen desorbed as a function of temperature could be derived. Validity of this technique has been confirmed in our previous work [13].

The surface characteristic of sample was examined by X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES), which was performed with a PHI

Table 1 The characterization and phase composition of the samples

Sample number	Characterization	Phase composition
1	HCS product	Mg_2NiH_4, $Mg_2NiH_{0.3}$
2	Dehydrogenated sample 1	Mg_2Ni
3	Air exposed sample 2 for 5 min	Mg_2Ni
4	Fully hydrogenated sample 2	Mg_2NiH_4
5	Air exposed sample 4 for 5 min	Mg_2NiH_4

550 EACA/SAM photoelectron spectrometer using Al Kα (1486.6 eV) radiation. The C1s peak of contaminated carbon at 284.6 eV was used to calibrate the peak positions of XPS. Electron gun voltage of 3 kV and argon ion gun voltage of 4 kV were selected for AES. The sputtering area of argon ion was 2×2 mm^2.

Results and discussion

Hydriding properties

Figure 1 shows the hydriding curves of samples 2 and 3 in the first hydriding process at 603 K and 3.0 MPa. It can be seen that the hydriding activity of sample 2 is so high that saturated content of hydrogen can be absorbed in the first hydriding process and 90% of maximum hydrogen storage capacity can be reached within 300 s, which is similar to the result as reported in [11]. In contrast, the hydriding activity of sample 3 decreases obviously. It can't absorb saturated content of hydrogen in the first hydriding process. On the other hand, the hydriding rate is very slow. For example, the time needed for absorbing 3.0 wt.% of hydrogen for sample 2 is less than 250 s. However, it takes more than 1500 s for sample 3, which is six times of sample 2. It should be reminded that the only difference of the preparation conditions between samples 2 and 3 is that sample 2 was never exposed to air, whereas sample 3 was exposed to air for durations of about 5 min. The different hydriding properties of samples 2 and 3 indicate that the exposure to air has a significant effect on the hydriding activity of Mg$_2$Ni, the as-dehydrogenated HCS product of Mg$_2$NiH$_4$.

It was reported that the decrease in particle size and the generation of many tree-like nano-order fissures happens during the first dehydriding process of the HCS product of Mg$_2$NiH$_4$ [12, 14], which brings about a widely distributed fresh surface to sample 2 consequently. When sample 2 is exposed to air, however, the fresh surface generated will be oxidized. The result suggests that it is the surface oxidation that makes the hydriding activity of the as-dehydrogenated HCS product of Mg$_2$NiH$_4$ decreased. When the operation temperature and hydrogen pressure of the first hydrogenation for samples 2 and 3 decreased to 553 K and 1.5 MPa, respectively, the negative effect of air-exposure or surface oxidation on the hydriding activity become more serious. As shown in Fig. 1, the hydriding rate of sample 3 is much lower than that of sample 2, and the hydrogen content at the end of the hydriding process of sample 3 is only 2.58 wt.%.

Dehydriding properties

The amounts of hydrogen desorbed as a function of temperature during heating samples 1, 4 and 5 in vacuum are shown in Fig. 2. The dehydriding onset (the temperature at which hydrogen begins to release from the hydride) of samples 1 and 5 is about 540 K. In comparison, the dehydriding onset of sample 4 is about 450 K, which is 90 K lower than that of samples 1 and 5. Since samples 1 and 5 were air-exposed prior to dehydrogenation, while sample 4 never contacted with air, it is indicated that the air-exposure or surface oxidation unambiguously limits the hydrogen release of the hydride, whether for the
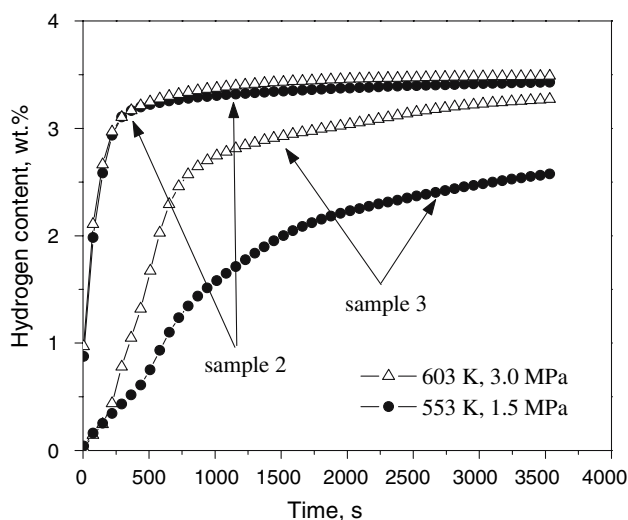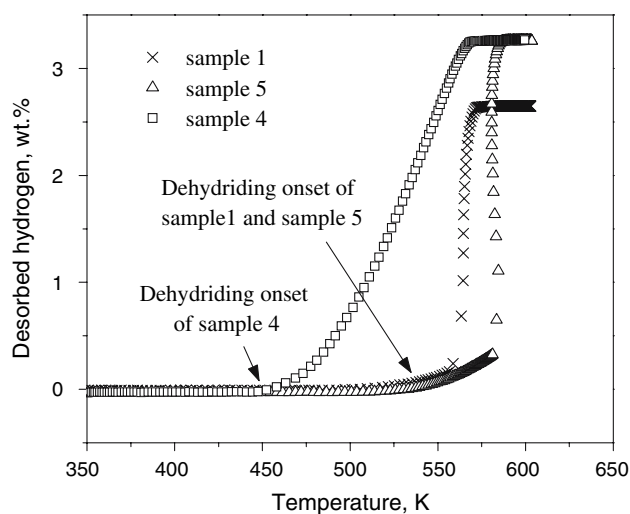

Fig. 1 The influence of air exposure on the hydriding activity. Hydriding curves of Mg$_2$Ni unexposed to air (sample 2) and air exposed for 5 min (sample 3) in the first hydriding process at 603 K and 553 K, respectively

Fig. 2 The influence of air exposure on the hydrogen desorption. Plots of the desorbed hydrogen amount vs. temperature for fully hydrogenated Mg$_2$Ni unexposed to air (sample 4) and corresponding samples exposed to air for 5 min (samples 1 and 5)

as-synthesized HCS product (sample 1) or the fully hydrogenated HCS product (sample 5) that experienced one dehydriding–hydriding cycle.

AES and XPS analyses

Figure 3 shows the AES depth profiles of atomic concentration percentage of sample 3, which was obtained by the sensitivity factor method. On the top surface, the element Mg and O are dominant, whereas the relative concentration of Ni is very low. For example, the molar ratio of Mg:Ni is about 30:1 before sputtering, which is much larger than the total ratio of 2:1 for sample 3. With the increasing sputtering time, the amount of Mg and O decreases gradually, together with the obvious increase in the concentration of Ni. While upon sputtering for about 1100 s, the Mg:Ni ratio becomes smaller than 2:1, corresponding to the beginning of enrichment of Ni. The results implies that the selective oxidation and surface segregation of Mg must happen on the surface of sample 3, and the surface of sample 3 can be regarded as composed of the top surface enriched with Mg and the layer underneath the top surface enriched with Ni. This surface structure is similar to that of an amorphous MgNi alloy investigated by Zhang et al. [15]. Although the surface segregation can be considered as one of the most important mechanisms involved in the surface activation of hydride forming alloys [16], it is disadvantageous for the hydriding and dehydriding as compared with the flesh surface based on the results described in sections "Hydriding properties" and "Dehydriding properties."
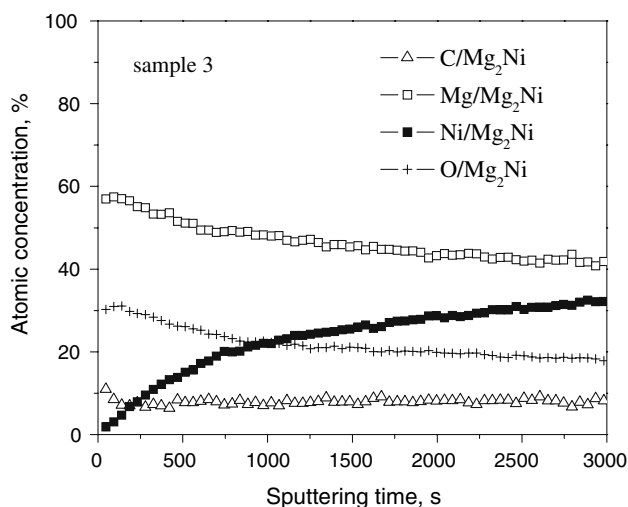
Figure 4 gives the XPS wide-scan spectrum and Mg 2p narrow-scan spectrum of sample 3. As shown in the figure, the peaks corresponding to Mg, O and C are observed easily, while the Ni peaks are hardly found, which is consistent with the observation of AES. The binding energy of Mg 2p peak is 49.4 eV. Since the standard binding energy of Mg in $Mg(OH)_2$ and MgO are 49.5 eV and 50.8 eV, respectively, it can be considered that the Mg on the outmost surface of sample 3 exists mainly in the state of $Mg(OH)_2$.

Discussion

In general, the hydriding rate of Mg_2Ni alloy is controlled by at least three factors [17]: (1) the rate of hydrogen molecule dissociation into hydrogen atoms on the surface, which is usually catalyzed by transitional metal Ni; (2) the rate of hydrogen atoms penetrating the surface into the bulk of alloy; (3) the ability of hydrogen diffusion in the alloy and formation of hydride. For sample 3 studied in this paper, hydrogen molecules must dissociate on the oxidized surface, and the dissociated hydrogen atoms must penetrate the surface hydroxide layer into the bulk, which causes the additional energy barrier of these two steps. As a result, the hydriding activity of sample 3 is greatly limited as shown in Fig. 1. In comparison, due to the fresh surface generated during the first dehydriding process of the HCS product of Mg_2NiH_4 and without an exposure to air, sample 2 catches hydrogen easily. From this point of view, the first dehydriding process of the HCS product is most important for getting the high hydriding activity. This methodology can
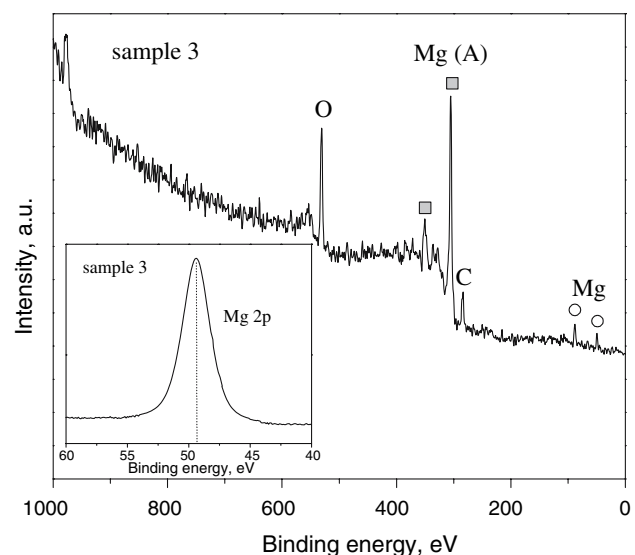

Fig. 3 AES depth profiles of atomic concentration percentage of sample 3 (air exposed sample 2)

Fig. 4 XPS wide-scan spectrum of the outmost surface of sample 3 (air exposed sample 2). Inset shows the Mg 2p narrow-scan spectrum

be applied to the other hydrogen storage alloys. That is, storage or transportation of hydrogen storage alloys in the state of hydride instead of alloy.

The hydrogen desorption is the reverse process of hydrogen absorption. Similar considerations can be applied to determine the controlling factors for hydrogen desorption. While the surface of Mg_2Ni hydride is covered with a hydroxide layer, the ability of hydrogen atoms penetrating the surface to the exterior and recombining into hydrogen molecules will certainly decrease. As a result, the dehydriding properties of samples 1 and 5 is much lower than that of sample 4 as shown in Fig. 2, due to the formation of a surface hydroxide layer in the process of air-exposure.

Conclusions

In this paper, the samples corresponding to different hydrogenation–dehydrogenation stages and air-exposed states of the HCS product were prepared, and the relationship between surface oxidation and hydriding–dehydriding properties of the HCS product was investigated systematically. The results indicated that the hydriding properties of the as-dehydrogenated HCS product of Mg_2NiH_4 and the dehydriding properties of the HCS hydride are both influenced obviously by the treatment of air-exposure, these are the decreased hydriding activity and the increased dehydriding temperature, respectively. The Mg segregation and the formation of hydroxide layer on the top surface of the air-exposed samples are the main reasons for the decreased hydriding and dehydriding properties. The generation of fresh surface during the first dehydriding process was confirmed to be most important for the high activity of the HCS product of Mg_2NiH_4.

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