Effect of Ball-Milling on the Properties of Mg$_2$Cu Hydrogen Storage Alloy

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We investigated by differential scanning calorimetry the effect of ball milling on the hydrogenation properties of Mg$_2$Cu, a hydrogen storage alloy, prepared by two methods: One is mechanically alloyed Mg$_2$Cu using Mg and Cu powders as starting materials. Eight hours (= 28.8 ks) of ball milling transformed the Mg : Cu = 2 : 1 mixture into Mg$_2$Cu single phase which reacts reversibly with hydrogen. The other is prepared by ball milling a cast Mg$_2$Cu alloy. While the as-cast Mg$_2$Cu undergoes neither hydrogenation nor dehydrogenation under 3 MPa of hydrogen in the temperature range of 300–773 K, just an hour of ball milling activates the inert Mg$_2$Cu to react with hydrogen reversibly. Examining the milling period dependency of the particle size, crystallite size, activation energy and the apparent heat of dehydrogenation which reflects the fraction of activated part in a specimen, we found that the ball milling firstly influenced the particle size and the activated fraction of the sample, and then followed the effect on the crystallite size and kinetic properties. We also found that a trace amount of oxygen could significantly spoil the benefits brought by the ball milling for longer period of milling. [doi:10.2320/matertrans.MRA2008183]

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1. Introduction

Hydrogen is considered an energy carrier for the twenty-first century. For practical application of hydrogen energy system, storing and transporting hydrogen safely and efficiently is a big technical challenge. Reilly and Wiswall$^1$ pioneered the research field of ‘hydrogen storage alloy’ by preparing Mg$_2$Cu by means of melting method and found that Mg$_2$Cu disproportionately reacts with hydrogen as:

$$\frac{2}{3} \text{Mg}_2\text{Cu} + \text{H}_2 \leftrightarrow \text{MgH}_2 + \frac{1}{3} \text{Mg}_2\text{Cu}_2,$$ (1)

Comparing this system with pure Mg, one notices that, whereas the hydrogenated entity in this system is MgH$_2$, the dehydrogenated state is not pure Mg but Mg$_2$Cu. This difference in the dehydrogenated state brings the difference in the thermodynamic properties: The dissociation temperature under 0.1 MPa(H$_2$) for reaction (1) is 512 K,$^{11}$ while that of pure Mg is 559 K. The reaction kinetics of Mg$_2$Cu-H$_2$ system is also different from Mg-H$_2$ system as reflected in their activation energies$^3$ (Mg-H$_2$: 289 ± 5 kJ·mol$^{-1}$, Mg$_2$Cu-H$_2$: 200 ± 5 kJ·mol$^{-1}$).

Recently Ueda et al. prepared Mg$_2$Cu by means of the repetition rolling and observed the pressure plateau at 0.05 MPa in both hydrogenation and dehydrogenation at the equilibrium temperature as low as 473 K$^{13}$ at which temperature Reilly et al. was not able to determine the isotherm due to the slow kinetics. The study by Ueda et al. proved that a morphological modification in alloys could significantly improve the hydrogenation properties of disproportionate Mg$_2$Cu system.

In the present article, we distinguish the terms ‘mechanical alloying’ (abbreviated as MA hereafter) and ‘mechanical grinding’ (MG): The former is used when we start ball-milling using a mixture of Mg and Cu powder while the latter is used when we start with Mg$_2$Cu powder. The main objective of the present study is to investigate the effect of ball-milling on the mechanically ground Mg$_2$Cu alloy (MG sample) in terms of the ‘activated’ fraction of the sample, particle size, crystallite size and activation energy with respect to the milling period. But before that, we also show that Mg$_2$Cu intermetallic compound can be synthesized by mechanically alloying the Mg and Cu powder (MA sample). For both MA and MG samples, the hydrogenation and dehydrogenation properties were examined by means of the differential scanning calorimetry (DSC).

2. Experimental

Starting materials, Mg$_2$Cu powder (99.9%), Mg powder (180 µm, 99.9%) and Cu powder (180 µm, 99.9%) were purchased from Kojundo Chemical Lab, Co. Ltd. To avoid oxidation, powders were handled in a glove box filled with Ar whose dew point is maintained below 200 K and oxygen concentration below 1 ppm. We weighed out 3 g of powder for each batch of ball milling. In case of MA, prior to the ball-milling we mixed Mg and Cu powder using an agate mortar in such a way that the molar ratio of Mg and Cu be 2 : 1. Planetary ball-mill used in the present study is a Fritsch P6. The grinding vessel (inner volume 80 cm$^3$) and 22 balls (ø10 mm) are made of hardened stainless steel. The rotation speed was 300 rpm. The milling vessel was filled with 0.1 MPa of Ar during the milling. Rotation was paused for 900 s after every 1800 s of milling in order not to raise the temperature of the sample too much. In this article, samples are labeled according to the milling period; for example, ‘MG-3.6 ks’ stands for the sample prepared by milling Mg$_2$Cu powder for 3.6 ks, ‘MA-28.8 ks’ for the sample prepared by milling Mg and Cu mixture for 28.8 ks and so on.

In order to identify the constituent phases and to observe the microstructure, we used a powder X-ray diffractometer (XRD, Rigaku RINT2000, Cu-K$\alpha$ radiation) and a scanning electron microscope (SEM, JEOL JSM-6301F) equipped with an energy dispersive spectrometer (EDS, Oxford Instruments LINK ISIS). The XRD was operated at the fixed time...
(FT) mode. Diffraction angle (2θ) was measured in the range of 10–120° with 0.05°-step and integration time of 3 s per step. We mixed Si powder (Sigma Aldrich, 99.9995%) with samples for the diffraction angle correction. We estimate the crystallite size from the XRD peak width based on the Scherrer equation. The peak width is corrected by measuring the XRD of a quartz powder whose crystallite size is considered infinite.

The hydrogenation and dehydrogenation properties were investigated by a DSC (Rigaku DSC-8230HP) under 3 MPa of hydrogen atmosphere from 313 to 673 K with heating rate of 5 K·min⁻¹ unless otherwise stated. For each run of the DSC measurement, 70 mg of the sample was sealed in an Al crucible in the glove box. A pinhole was punctured with a needle on the lid of the Al crucible just before the crucible is loaded in the DSC. To convert observed nominal heat into the real caloric value, the apparatus was calibrated by measuring the heat of dehydrogenation of pure MgH₂ (ΔHf/H₂ = 74.5 kJ·mol⁻¹).

To see the relation between the hydrogenation properties and particle size, we measured the mean particle size of sample powder with a laser diffraction particle size analyser (Shimadzu SALD-2000). Ethanol was used as a suspending fluid.

The influence of oxidation was investigated by determining the oxygen concentration in the sample by an oxygen and nitrogen analyzer (Horiba EMGA). The sample was sealed in a Ni capsule in the glove box. The apparatus was calibrated with standard Ti tablets (Alpha Resources) whose oxygen concentration is certified to be 1913 ± 65 ppm as well as with an empty Ni capsule as a blank run.

3. Results and Discussion

3.1 MA sample

To synthesize Mg₂Cu alloy, Sun et al. proved that ball-milling was an effective pre-treatment for the sintering synthesis. Ball-milling was also applied by Cao et al. to synthesize directly, i.e. without further treatment, a Mg12.1 mass%-Cu composite which is composed of Mg and Mg₂Cu phases. Reports on obtaining pure Mg₂Cu only by ball-milling have been rare, but in 2007 Jurczyk and Szajek et al. succeeded in synthesizing Mg₂Cu alloy by mechancial alloying. Here we also tried to synthesize pure Mg₂Cu alloy starting from Mg and Cu powders by ball-milling.

Figure 1 shows the XRD profiles of the MA sample. Signals from Mg₂Cu grow stronger as the ball milling proceeds. For 28.8 ks of milling, the Mg₂Cu phase appears prominently and no signal from other phase is observed. Longer milling period than 28.8 ks leads to the broadening of diffraction peaks. The milling period necessary to obtain Mg₂Cu phase, 28.8 ks = 8 h, and the crystallite size calculated based on the Scherrer equation, ~10 nm, are comparable to those of Jurczyk’s study (18 h and 30 nm, respectively).

A SEM topograph of MA-28.8 ks is shown in Fig. 2. The compositions in atomic percentage analyzed by the EDS at the spots indicated by numerals in the topograph are respectively: (1) Mg 61.8, Cu 38.2; (2) Mg 70.5, Cu 29.5 and (3) Mg 41.6, Cu 58.4. As shown in the XRD (Fig. 1), the majority of MA-28.8 ks comprises Mg₂Cu phase, but as in the spot (3) in Fig. 2, a trace of the sample contains a Cu-rich phase, which does not give an observable intensity in the XRD.

As shown in §3.3 DSC, the MA sample undergoes reversible hydrogenation and dehydrogenation reactions.

3.2 MG sample

MG sample was prepared under the same milling conditions as the MA sample. Although the starting Mg₂Cu phase persists without decomposing into other phase, broadening of XRD peaks becomes prominent for the milling period longer than 28.8 ks as in the case for the MA sample.

3.3 DSC

MG-0, the starting material for MG, does not react with hydrogen at all under the present conditions of DSC (3 MPa(H₂), 313 to 673 K). All the other samples prepared and treated in the present study show reversible thermal effects corresponding to the hydrogenation and dehydrogenation. For MA-28.8 ks, the mean value of onset temperatures of exothermal hydrogenation and endothermic dehydrogenation is 633 K, and that for MG-3.6 ks is 654 K. These temperatures and hydrogen pressure of 3 MPa coincide with
those extrapolated from the van’t Hoff relation described in Reilly’s study, indicating that the samples obtained in the present study have the same thermodynamic properties as theirs. Figure 3 shows the cycle dependency of the ‘apparent’ heat of dehydrogenation $Q$ calculated from the endothermic peak area of DSC. If the sample reacted completely according to reaction (1), the heat of dehydrogenation $\Delta H$ should be 974 J g$^{-1}$ which is calculated from the slope of the van’t Hoff relation. That the observed ‘apparent’ heat of dehydrogenation $Q$ does not reach this value can be interpreted as the incompleteness of the reaction. (Notice that the heat measured by means of calorimetry is per specimen, whereas the heat of reaction calculated from the van’t Hoff relation is per unit amount of H$_2$ no matter how much sample reacts with hydrogen.) For example, MG-3.6 ks shows at the second cycle the largest value of $Q/Jg^{-1} = 800$ which is 82% of $\Delta H/Jg^{-1} = 974$, namely, about 20% of the sample does not react with hydrogen as if it is not ‘activated’ by the ball-milling. Thermal gravimetry also shows that the mass of desorbed hydrogen is about 80% of the theoretical value based on reaction (1). Remaining ca. 20% is too large to be attributed to the impurities alone. In case of MA-28.8 ks, the activated part is smaller still than MG-3.6 ks, which maybe related to the longer milling period (see §3.5 Oxides contamination). In the equilibrium hydrogen pressure measurement by Reilly et al., one can see the incomplete reaction with 10–20% of deficiency in hydrogen content from the theoretical value. Similarly, reversible hydrogen content of sodium aluminium hydride, NaAlH$_4$, which desorbs hydrogen and decomposes disproportionately to NaH and Al, seldom exceeds 90% of the theoretical value. Reversible disproportionate hydrogen storage materials, such as Mg$_2$Cu or NaAlH$_4$, commonly suffer from this incompleteness in reaction presumably due to the long distance of diffusion of multiple solid phases during the reaction. Aside from the incompleteness of the reaction, all the prepared Mg$_2$Cu samples show good reversibility at least for a couple of cycles.

3.4 Effect of milling period on MG sample

Figure 4 shows the variations in the apparent heat of dehydrogenation $Q$, the crystallite size $L$, the activation energy of dehydrogenation $E_a$ and the particle size $D$ with respect to the milling period $t$ for the MG samples. $Q$’s are calculated from the DSC peak area at the second cycle of dehydrogenation, $L$’s from the width of the XRD peak at $2\theta = 37^\circ$ which is free from overlapping, $E_a$’s from the peak temperature shift in DSC based on the Kissinger method with changing the heating rate and $D$’s from the laser diffactrometry. Figure 4 indicates that, as milling proceeds, $Q$ increases and $E_a$, $L$ and $D$ decrease monotonously. As mentioned in §3.3 DSC we assume that $Q$ reflects the fraction of the specimen that is activated to react with hydrogen by ball milling. Although for shorter milling period $E_a$ seems to be too large as a physically relevant value, we consider $E_a$ reflects the kinetic properties of the material. If we express these variations in terms of exponential decay function, i.e. $y = A + B \exp(-t/\tau)$, the time constants $\tau$ for $Q$, $D$, $E_a$ and $L$ are respectively 0.20, 0.14, 0.72 and 1.83 ks. (To determine $\tau$ for $D$ and $L$, the results of MG-28.8 ks, which are not shown in Fig. 4, are included.) These time constants roughly suggest that the ball milling firstly brings the decrease in the particle size and the increase in the activated fraction of the material, and then follows the slower decrease in the crystallite size which seems to be related to the kinetic properties reflected in the activation energy. Because the decrease in the particle size $D$ amounts to the increase in the surface area, the present observation suggests that the activation process of Mg$_2$Cu, reflected in $Q$, is related to the surface of particles. That is, a particle becomes reactive with hydrogen when its surface is activated by the ball milling.

3.5 Oxides contamination

Returning to Fig. 3, one finds the apparent heat of dehydrogenation $Q$ for MG-28.8 ks is smaller than that of MG-3.6 ks. Further extension of milling period to 86.4 ks led to $Q/Jg^{-1}$ $\sim$ 130. Oxygen concentration analysis revealed that, while the starting materials and MG-3.6 ks contain less than 100 ppm of oxygen, MA-28.8 ks and MG-28.8 ks contain about 300 ppm, and MG-86.4 ks contains as high as 1500 ppm. Albeit highly contaminated, these oxygen concentrations do not match the 20%-deficiency in reaction reflected in the smaller $Q$ values (see §3.3 DSC).
incompleteness of the reaction may be explained by the presence of oxides that cover the surface of particles and hinder the reaction with hydrogen. This speculation is consistent with the above mentioned discussion on the relation between the particle size $D$ and the apparent heat of dehydrogenation $Q$.

We handled the material not to expose to oxygen whole through the experiment. Oxygen, a trace amount of which may be present in the glove box, in the pipeline gases or on the surface of the milling vessel and balls, contaminated the sample nevertheless. We recognize afresh the importance of a stricter oxygen control in handling a highly reductive material such as Mg.

4. Conclusions

(1) Mg$_2$Cu, a hydrogen storage alloy first investigated by Reilly et al., was successfully prepared by mechanically alloying Mg and Cu powders for 28.8 ks (= 8 h). Thus prepared Mg$_2$Cu (MA-28.8 ks) reversibly reacts with hydrogen.

(2) While the as-cast Mg$_2$Cu powder does not react with hydrogen at all, just an hour of milling activates the sample leading to the reversible hydrogenation and dehydroganation (MG-3.6 ks).

(3) The effect of ball milling appears first as the decrease in particle size $D$ and the increase in the activated fraction of the material which is reflected in the apparent heat of reaction $Q$. Then follows the decrease in crystallite size $L$ which improves the reaction kinetics reflected in the activation energy $E_a$.

(4) The benefits brought by the ball milling can be vitiated by a trace amount oxygen if you elongate the milling period too much.

REFERENCES