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Mg_2Ni hydride electrodes prepared by sintering and subsequent ball milling with Ni powders

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Abstract

Mg_2Ni alloy electrodes were manufactured by a powder metallurgical technique followed by ball milling with Ni powders. The discharge capacities of the electrodes were significantly improved by ball milling. An amorphous structure is a key factor in order to achieve high discharge capacities. Other effective methods include increasing the ball milling time and changing the ratio of ball to sample weight.

Keywords: Ball milling; Amorphous; Mg_2Ni Alloy; Ni–MH Electrode

1. Introduction

Mg-based hydrogen storage alloys possess very high hydrogen absorption capacity. Magnesium is also abundant in nature, light in weight and low in cost. As a result, Mg_2Ni-type hydrogen storage alloys are promising energy conversion and storage materials. For a long period, it has been thought that Mg_2Ni-type hydrogen storage alloys, unlike $LaNi_5$-type hydrogen storage alloys, were unsuitable for Ni–MH negative electrodes because of their slow hydriding/dehydriding kinetics at ambient temperature and their oxidation in alkaline solution. In recent years, some research work on the properties of Mg_2Ni-type alloys has shown that they are promising materials for increasing the negative electrode capacity of Ni–MH batteries. The theoretical discharge capacity of Mg_2Ni alloy is approximately 1000 mAh/g, much higher than that of the main commercial $LaNi_5$ alloy (which has a capacity of only about 370 mAh/g).

The addition of other elements can increase the discharge capacities of Mg_2Ni electrodes. Cui and co-workers [1] reported a discharge capacity of 150 mAh/g for $Mg_{1.9}Al_{0.1}Ni_{0.9}Y_{0.1}$ alloy compared with only 8 mAh/g for Mg_2Ni alloy at a discharge current density of 5 mA/g. Microencapsulation of Mg_2Ni-type alloys by metal and alloy coatings can also improve the electrode performance. Luo and Cui [2] increased the discharge capacity of $Mg_{1.9}Al_{0.1}Ni_{0.9}Y_{0.1}$ alloy to ca. 175, 200 and 230 mAh/g at a current density of 10 mA/g by microencapsulation with Ni–B, Ni–P, and Ni–Pd–P respectively. The discharge capacity of the bare $Mg_{1.9}Al_{0.1}Ni_{0.9}Y_{0.1}$ alloy was only 140 mAh/g at the same discharge current density.

Lei et al. obtained improved discharge capacities of around 500 mAh/g for Mg–Ni alloys prepared by mechanical alloying (MA) at a current density of 20 mA/g [3,4]. Iwakura et al. [5] have also improved the discharge capacity of MA Mg-based alloy with graphite surface modification by ball milling (BM). After surface modification with Ni powder by ball milling, Kohno et al., have obtained large discharge capacities of 750 mAh/g at a discharge current density of 20 mA/g for modified Mg_2Ni alloys [6,7]. In our previous work [8], we fabricated a $Mg_{1.9}Al_{0.1}Ni_{0.8}Co_{0.1}Mn_{0.1}$ alloy ball milled with Ni powder and obtained its discharge capacity of 630 mAh/g at a discharge current density of 50 mAh/g.

Mechanical alloying and milling appear to be effective ways to achieve very high discharge capacities for Mg-based hydrogen storage alloys. The preparation processes of mechanical alloying and/or milling are very flexible, allowing different preparation conditions to affect the alloy structure and electrode properties. In this paper, we have tried to find a relationship between some of these factors and the properties of the Mg_2Ni alloy electrodes.

2. Experimental

The Mg_2Ni alloys were prepared by sintering Mg (50 mesh, 99.8%) and Ni (100 mesh, 99.7%) powders in their

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Table 1
Sintering conditions for two Mg_2Ni alloy samples

Sample name	Sintering conditions
Mg_2Ni alloy I	700°C 10 h
Mg_2Ni alloy II	700°C 10 h plus 900°C 0.5 h

required proportions under an argon atmosphere at 700°C for 10 h (alloy I) and 700°C for 10 h plus 900°C for 0.5 h (alloy II). Mechanical milling was performed with a Fritsch planetary ball mill. The vial and balls were made from stainless steel and hardened steel respectively. Mg_2Ni alloy and pure Ni powder were then mixed and milled in an argon atmosphere. The weight ratios of ball to sample were 30:1 and 100:1, respectively. After each specified number of hours of milling, the milled powders were examined by X-ray diffraction (XRD).

X-ray diffraction was conducted using a Philips PW1010 X-ray diffractometer with Cu Kα radiation. Morphology and electronic diffusion of the powders of ball milled Mg_2Ni alloys were carried out using a JEOL 2000 FX transmission electron microscope (TEM).

For the preparation of an electrode, the ball milled Mg_2Ni alloys were mixed with Ni powder (as a conductor) in the weight ratio of 1:1. The hydride electrodes were fabricated by mixing the resultant powders with polyvinyl alcohol (PVA) solution and pasting them onto a foamed nickel matrix which acted as the current collector for the electrode. The electrodes were then compressed at a load of 40 MPa for 1 min. The electrodes were immersed as negative electrodes in a 6 M KOH solution together with a counter electrode of sintered nickel. A mercury oxide electrode (Hg/HgO) was used as the reference electrode. The electrochemical charge–discharge properties of the ball milled Mg_2Ni alloys were measured using a battery test instrument. In the charge–discharge cycle tests, the charge cycle was commenced using a current density of 100 mA per gramme of hydrogen storage alloy for 12 h, then after a minute rest, the discharge was continued using a current density of 50 mA/g until the voltage of the negative electrode against the mercury oxide electrode reached −0.5 V. The discharge capacities of the BM alloys were calculated based on the amount of Mg_2Ni.

3. Results and discussion

3.1. Effect of the sintering process on the properties of Mg_2Ni alloy electrodes

Table 1 lists the sintering processes for two Mg_2Ni alloy samples. The X-ray diffraction patterns of Mg_2Ni alloy I and II are shown in Fig. 1. Both of the Mg_2Ni alloys have mainly Mg_2Ni phase but the alloy II has a small amount of an unknown phase. This is probably due to the high temperature of 900°C used in the sintering of alloy II. Fig. 2(a,b) shows the X-ray diffraction patterns of Mg_2Ni alloys I and II after ball milling for 50 and 60 h, respectively. The ratio of ball to sample weight was 30:1. Alloy II after ball milling for 60 h has mainly an amorphous structure while alloy I after ball milling for 50 h still shows some Ni phase. Fig. 3 shows the TEM image and corresponding electron diffraction of alloy II which are typical amorphous morphology and diffraction patterns. In Fig. 3(a), a marker indicates a particle which has amorphous structure. The discharge capacities as a function of cycle number for alloy I after ball milling for 50 h and alloy II after ball milling for 60 h are presented in Fig. 4. The initial discharge capacity of BM alloy I (422 mAh/g) is larger than that of BM alloy II (322 mAh/g). This result suggests Mg_2Ni alloys that it is better to select the lower sintering temperature for high discharge capacity of sintered Mg_2Ni alloys. Even so, the initial discharge capacity of the Mg_2Ni alloy ball-milled with Ni powder is still much larger than

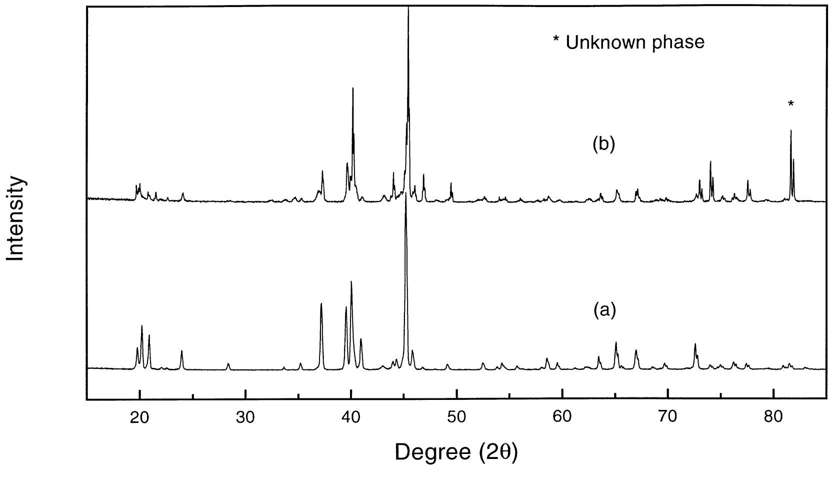

Fig. 1. X-ray diffraction patterns of Mg_2Ni alloys I (a) and II (b).

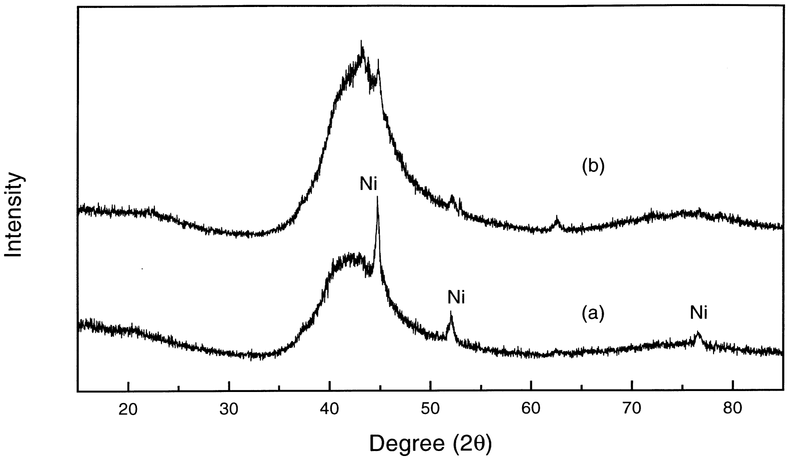

Fig. 2. X-ray diffraction patterns of Mg_2Ni alloys. (a) alloy I after ball milling for 50 h; (b) alloy II after ball milling for 60 h.

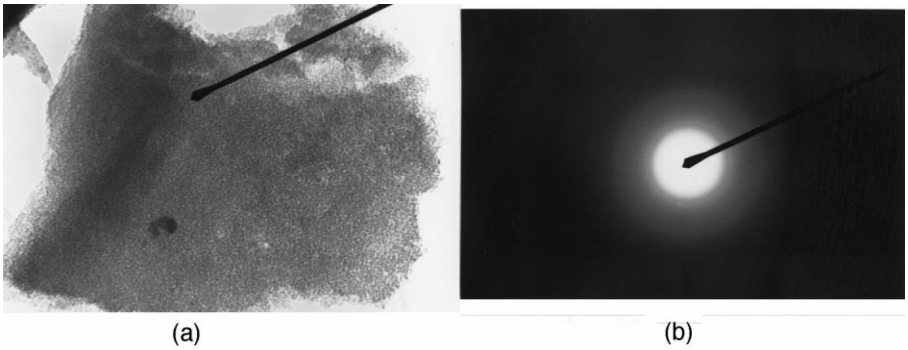

Fig. 3. TEM image (a) and corresponding electron diffraction (b) of alloy II after ball milling for 60 h.

that of the bare and microencapsulated $Mg_{1.9}Al_{0.1}Ni_{0.9}Y_{0.1}$ alloys previously reported [2]. It is known that amorphous alloys have excellent electrocatalytic activity [9] and corrosion resistance behaviour [10]. Thus, the amorphous structure of Mg-type alloy is a key factor to achieve a large discharge capacity.

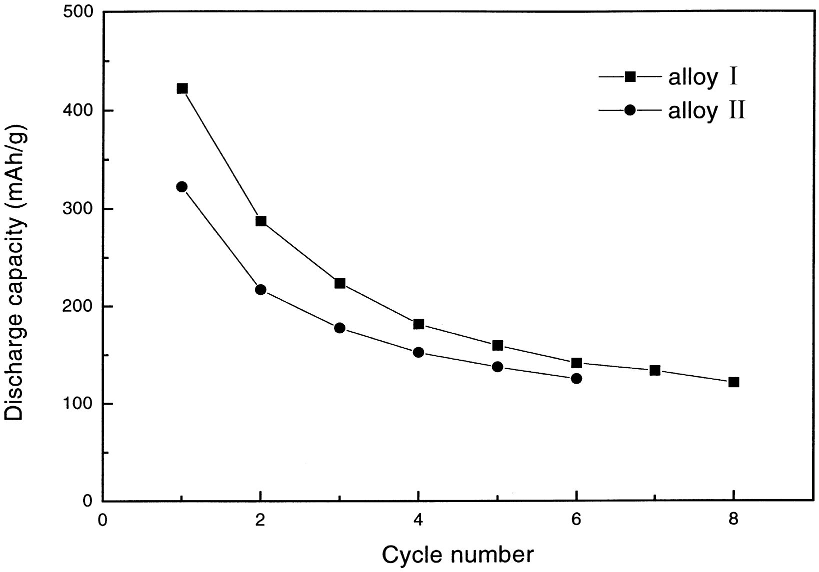

Fig. 4. Discharge capacities as a function of cycle number for alloys I after ball milling for 50 h and alloy II after ball milling for 60 h.

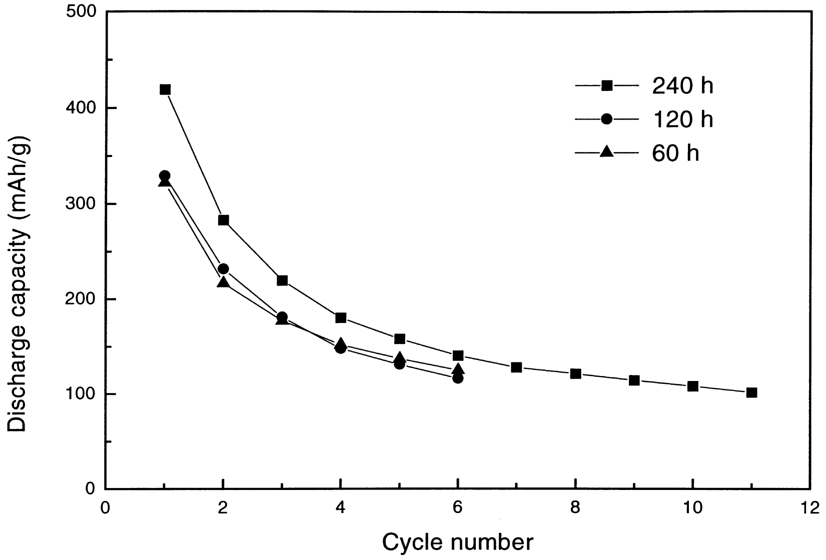

Fig. 5. Discharge capacities as a function of cycle number for Mg_2Ni alloy II ball-milled for 60, 120 and 240 h.

3.2. The effects of the ball milling hours on discharge capacity

The discharge capacities of sample of alloy II after ball milling for 60, 120 and 240 h with Ni powders are shown in Fig. 5 as a function of cycle number. The discharge capacities after 60 and 120 h are almost identical (initial discharge capacity of the sample ball-milled 120 h was 329 mAh/g). The discharge capacity after BM 240 h is higher than that of the other two samples. Fig. 6(i–iv) shows the X-ray patterns of alloy II after ball milling for (i) 0; (ii) 60; (iii) 120; and (iv) 240 h. After ball milling for 60 h, it was seen from Fig. 3 that the structure of Mg_2Ni alloy is already mainly amorphous. After additional milling, the alloy structures after BM 120 h and BM 240 h were not obviously altered, but the discharge capacity of the BM 240 h alloy was higher than that of the others, (its initial discharge capacity was about 419 mAh/g). This could be due to the amorphous structure of the sample ball-milled for 240 h alloy became more uniform with the additional ball milling and its quantity of amorphous phase increased.

3.3. The effects of the ratio of ball to sample weight during ball milling

One of the most important parameters in BM process is the ratio of the ball to sample weight. Fig. 7 shows the discharge curves of Mg_2Ni alloy II after BM for 60 h at the ratios of ball to sample weight of 30:1 and 100:1. The 100:1 sample has a larger initial discharge capacity of 468 mAh/g and longer cycle life (the discharge capacity is ca. 146 mAh/g at the 10th cycle). The discharge capacity is

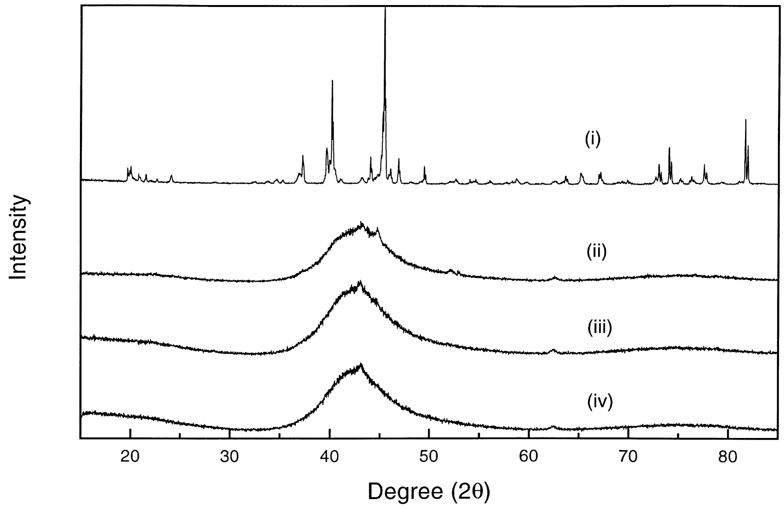

Fig. 6. X-ray diffraction patterns of the Mg_2Ni alloy II after ball milling time for: (i) 0; (ii) 60; (iii) 120; and (iv) 240 h.

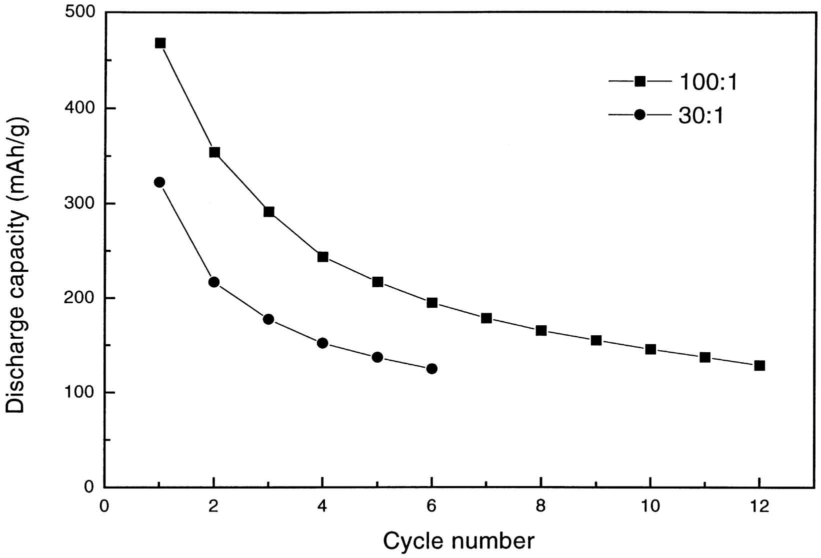

Fig. 7. Discharge curves of Mg_2Ni alloy II after ball-milled 60 h at the ratios of ball to sample weight of 30:1 and 100:1.

much higher than the initial discharge capacity of the corresponding sample where the ratio was 30:1 (322 mAh/g). This probably means that the higher ratio of ball to sample results in faster milling, so that a uniform amorphous structure is achieved more quickly.

In summary, all the ball milled Mg_2Ni alloy electrodes studied have shown improved initial discharge capacity but they degrade quickly upon cycling even when an amorphous structure is achieved. It was known that alloy degradation can be reduced by adding other elements [7,8]. A combination of elemental addition and ball milling appears to offer the prospect of further improvement in electrode performance.

4. Conclusion

Although conventional metallurgical techniques can be used to manufacture Mg_2Ni alloy electrodes, ball milling improves the discharge capacities of the electrodes significantly. The amorphous structure is a key factor in order to obtain high initial discharge capacities. Increasing the ball milling time and the ratio of ball to sample weight are effective methods to further improve the discharge capacity for Mg_2Ni alloys.

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