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Electrochemical properties of mechanically ground Mg_2Ni alloy

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Abstract

The electrochemical properties of Mg_2Ni type alloy powder prepared with a mechanical grinding (MG) of Mg_2Ni and Ni or Pd powders were investigated. This alloy powder was found to be mainly changed to an amorphous-like matrix with dispersed nano-size Ni or Pd particles by the MG treatment. As a result, the negative electrode of the mechanically ground Mg_2Ni alloy with Ni showed a large discharge capacity (830 mAh/g) which is 2.5 times larger than that of AB_5 type alloys. In the mechanically ground Mg_2Ni alloy with Pd, the cycle life of the alloy electrode was considerably improved. The effect of partial substitution on the hydrogen storage properties of Mg_2Ni was also investigated. It was found that the hydrogen reversibility of the mechanically ground $Mg_{1.9}M_{0.1}Ni$ (M=Al, B, C, Ag) alloy electrode was remarkably improved by the substitution of Mg with more electronegative elements.

Keywords: Hydrogen storage alloy; Mg_2Ni; Mechanical grinding; Electronegative element; Pd

1. Introduction

Nickel-metal hydride (MH) batteries using hydrogen storage alloys have attracted much attention because they have several advantages such as larger discharge capacity and higher tolerance of overcharge and overdischarge compared with nickel–cadmium batteries [1,2].

However, the capacity of an MH battery using $LaNi_5$ type alloy is approaching the limit, because the repeated improvements to increase cell capacity already realize very high utilization of the intrinsic capacity of the alloy. For increasing the cell capacity, Mg_2Ni alloy is one of the most favorable candidates. Mg_2Ni alloy is superior to $LaNi_5$ type alloy or Laves-phase alloys in material cost and theoretical hydrogen absorption capacity [3]. In particular, the theoretical discharge capacity of Mg_2Ni alloy is about 1000 mAh/g, which is ~2.7 times that of $LaNi_5$. One of the problems which prevent the application of Mg_2Ni for electrode material is that the hydrogen absorption and desorption reaction occurs only at high temperature (~200 to 300°C) [3], and the reaction rate is very slow even at high temperature. Several researchers have conducted investigations with a view to decreasing the absorption and desorption temperature of this alloy in a gas phase reaction [4–6]. Further, Mg-based alloys prepared by mechanical alloying (MA) have attracted the interest of workers seeking to increase the discharge capacity [7,8].

On the other hand, we studied the effect of mechanical grinding (MG) on the structural change and the hydrogen storage properties of this alloy [9–11]. In this work, in order to lower the hydrogen absorption temperature, the effect of partial substitution of several foreign elements (Al, B, C, Ag) for magnesium, combined with MG treatment, has been studied using electrochemical methods, and the structural change after MG treatment has been investigated to evaluate the applicability of this alloy system for MH battery.

2. Experimental

Mg_2Ni and $Mg_{1.9}M_{0.1}Ni$ (M=Al, C, B, Ag) alloy ingots were prepared by induction melting under argon gas at atmospheric pressure. These ingots were mechanically pulverized to 75 μm or less in diameter and preliminary activation with hydrogen was not performed. Mg_2Ni alloy powder and Ni powder were mixed in 1:x (x=0.5–3.0) molar ratio, and Mg_2Ni alloy powder and Pd powder were mixed in 1:1 molar ratio. Then the mixture was introduced with stainless steel balls (diameter: 10 mm) into a stainless steel vessel which was filled with Ar gas. After sealing, the vessel was subjected to an MG treatment for 100 h, at the rate of 200 rev./min. Crystallographic characterizations of the alloys were carried out by X-ray diffraction at room temperature, and the microstructures were also investigated with transmission electron microscopy (TEM).

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The hydrogen absorption–desorption properties of the alloy were investigated by an electrochemical charge–discharge process. The hydrogen storage alloy powder was mixed with electrolytic copper powder in the weight ratio of 1:3, then 1 g of this mixture was compressed in a tablet-molding apparatus (inner diameter: 10 mm) with a pressure of 10 tons for 5 min. This pellet was then interposed between Ni gauze, and the portion on the edge was tightly spot-welded to keep the electrochemical contact between the pellet and Ni gauze. Afterwards, a Ni lead wire was attached to Ni gauze by spot-welding to prepare a hydrogen storage alloy electrode (negative electrode).

The negative electrode and counter electrodes (sintered nickel) were dipped in an 8 M KOH, and then charge–discharge cycle tests were performed at 25°C. The mercury oxide electrode (Hg/HgO/8 M KOH) was used as a reference electrode. In these charge–discharge cycle tests, the charge was conducted using the current rate of 100 mA/g-hydrogen storage alloy for 10 h. After a 10-min rest, the discharge was conducted using the current rate of 20 mA/g-hydrogen storage alloy until the voltage of the negative electrode against the mercury oxide electrode reached −0.5 V.

3. Results and discussion

3.1. Hydrogen storage properties of MG-Mg_2Ni type alloy

In the case of $LaNi_5$ alloy, the Ni layer on the surface works as a catalytic site when hydrogen absorption occurs [2]. It is also reported that the hydrogen storage properties of $LaNi_5$ are improved by nickel plating [12] or alkali treatment [13]. For these reasons, we direct our attention to the formation of the nickel layer on Mg_2Ni alloy. Providing a charge–discharge reaction occurs between Mg_2Ni and Mg_2NiH_4, the theoretical capacity of this alloy electrode is 999 mAh/g. However, only a little capacity could be observed when the electrode was prepared with Mg_2Ni powder without any treatment [10]. Iwakura et al. [14] also reported that the discharge capacity of Mg_2Ni alloy at 30°C was very low. In the meantime, we reported that Mg_2Ni could absorb gas phase hydrogen if the nickel layer was formed on the alloy surface [9]. With a view to endow this alloy with much more nickel, we investigated the effect of mechanical grinding with Ni on Mg_2Ni alloy.

The cyclic trends of discharge capacities of MG-(Mg_2Ni+xNi) (x=1.0, 2.0, 3.0) alloy electrodes at 25°C are shown in Fig. 1. The discharge capacities of these MG alloys were revealed as those per unit gram of Mg_2Ni. The MG-(Mg_2Ni+2Ni) electrode had the discharge capacity of 830 mAh/g at the first cycle, which was equal to 83% of the theoretical capacity. The discharge capacity continuously decreased during the cycle test, and reached 430 mAh/g at the 20th cycle. In the case of MG-(Mg_2Ni+3Ni) alloy electrode, the discharge capacity of 420 mAh/g still remained at the 20th cycle, even though the first cycle capacity decreased to 600 mAh/g. These results clarified that the mechanical treatment was an effective way to improve the charge–discharge capability of the negative electrode containing Mg_2Ni alloy. Further, the reversibility was also improved with increasing quantity of added Ni.

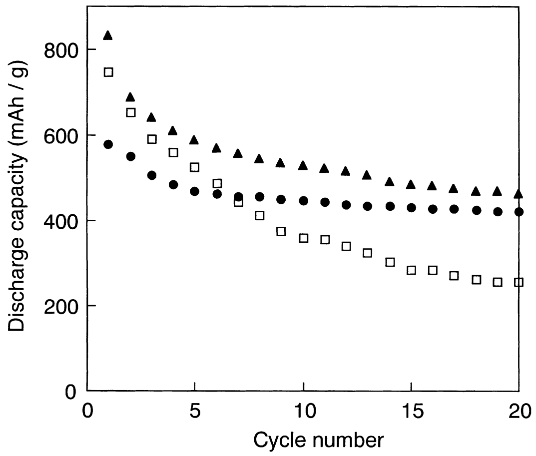

Fig. 1. Discharge capacity of MG-(Mg_2Ni+xNi) electrode (□) Mg_2Ni+1.0Ni; (●) Mg_2Ni+3.0Ni; (▲) Mg_2Ni+2.0Ni.

The discharge curves of the MG-(Mg_2Ni+xNi) (x=0.5, 1.0, 2.0) electrode are shown in Fig. 2. These curves had wide plateau regions during discharge, and any other potential step attributed to side reactions was not observed. These results suggested that only the hydrogen electrode reaction took place.

Plots of discharge capacity and average discharge potential as a function of the molar ratio of Ni to Mg_2Ni are shown in Fig. 3. The mechanically ground Mg_2Ni alloy electrodes had large discharge capacities, and the maximum capacity was achieved in the mixture of 1:2 (Mg_2Ni:Ni). In contrast, the average discharge potential continuously shifts in the negative direction with increasing Ni powder.

XRD patterns for MG-(Mg_2Ni+xNi) (x=1.0, 2.0, 3.0)

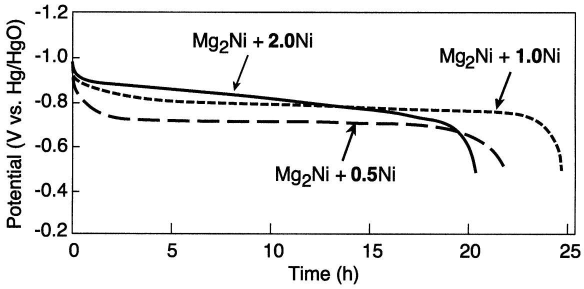

Fig. 2. Discharge curves of MG-(Mg_2Ni+xNi) electrodes. (Discharge rate: 20 mA/g Mg_2Ni.)

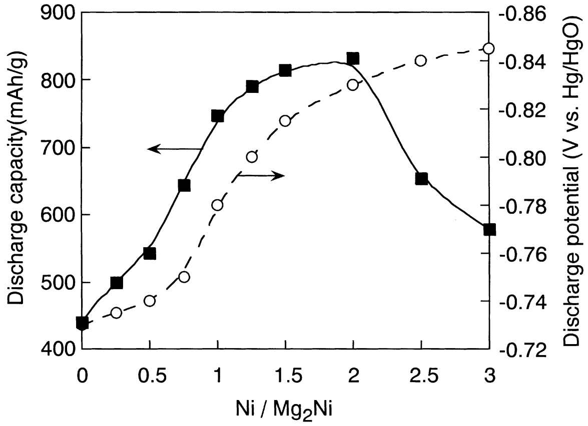

Fig. 3. Plots of discharge capacity and discharge potential as a function of Ni/Mg_2Ni. (Discharge rate: 20 mA/g Mg_2Ni.)

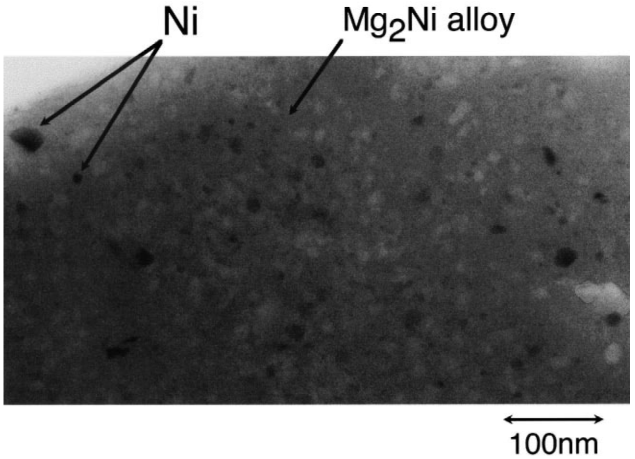

Fig. 5. TEM image of MG-(Mg_2Ni+Ni) alloy.

alloy are shown in Fig. 4. After mechanical grinding, the characteristic peaks of the Mg_2Ni phase decreased in intensity and broadened. This profile indicated that MG-Mg_2Ni type alloy had been mainly transformed to an amorphous-like state. The existence of the sharp diffraction peaks attributed to the nickel metal suggested that the nickel still remains in its crystal state.

In order to clarify the structural change after MG treatment, the microstructure of this alloy was examined by TEM. The TEM image of the MG-(Mg_2Ni+Ni) alloy powder is shown in Fig. 5. It was observed that the fine nickel spherical particles (~10 nm in diameter) were dispersed in Mg_2Ni alloy. This result clearly showed that the MG treatment was an effective method to prepare nano-nickel dispersed samples. Accordingly, when Mg_2Ni is mechanically ground with Ni, Mg_2Ni alloy was mainly transformed to an amorphous-like state, on the other hand, Ni was crushed to nano-size nickel particles and dispersed into amorphous-like matrix. By means of this structural change, the hydride stability in this alloy seemed to be decreased, and the electrode capacity remarkably increased at room temperature.

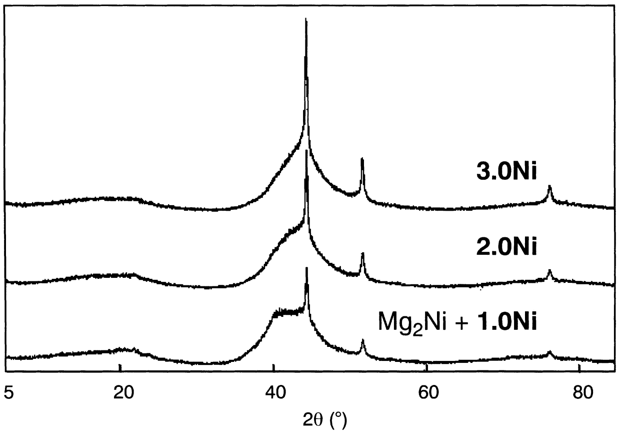

Fig. 4. XRD patterns of MG-(Mg_2Ni+xNi).

3.2. *Hydrogen storage properties of $Mg_{1.9}M_{0.1}Ni$ (M= Al, B, C, Ag) type alloy*

The effect of partial substitution of Mg with a foreign element on the reactivity with hydrogen was investigated. To reduce the polarization between Mg and Ni, the Mg was substituted with Al, B, C, Ag which are more electronegative (Al: 1.5, B: 2.0, C: 2.5, Ag: 1.9) than Mg (=1.2). Crystallographic characterizations of the partially substituted alloys were carried out by X-ray diffraction at room temperature. The results show that these alloys had Mg_2Ni-type hexagonal structures. After MG treatment, the characteristic peaks of these substituted alloys decreased in intensity and broadened. In our previous paper [11], we reported that $Mg_{1.9}Al_{0.1}Ni$ was capable of absorbing hydrogen at a lower temperature (80°C) than Mg_2Ni (150°C). This result suggested that substitution of more negative elements for some part of Mg was effective to lower the temperature for hydrogen absorption, while maintaining an excellent hydrogen absorption capacity.

The discharge capacities of MG-($Mg_{1.9}M_{0.1}Ni$+Ni) electrodes at 25°C are shown in Table 1. The capacity of

Table 1
Discharge capacity of MG-($Mg_{1.9}M_{0.1}Ni$+Ni) alloy electrode

M	C_{max} (mAh g^{-1})	C_{10th} (mAh g^{-1})
Mg	750	359
Al	690	491
B	688	430
Ag	622	405
C	746	431

these MG alloys was calculated based on the amount of $Mg_{1.9}M_{0.1}Ni$. The MG-(Mg_2Ni+Ni) electrode has a discharge capacity of 750 mAh/g at the first cycle. However, this capacity decreased to 359 mAh/g at the 10th cycle. In contrast, the capacity retention of MG-($Mg_{1.9}M_{0.1}Ni$+Ni) system at the 10th cycle was markedly improved, even though the capacities at the first cycle were lower than that of MG-(Mg_2Ni+Ni). In particular, in the case of MG-($Mg_{1.9}Al_{0.1}Ni$+Ni), the alloy electrode has the discharge capacity of 491 mAh/g at the 10th cycle, whereas the first cycle capacity reached to 690 mAh/g. By means of a partial substitution of more electronegative elements for Mg, the hydride stability in this alloy seemed to be decreased, indicating that it is possible to improve the reversibility. The effect was observed to be especially significant in the case of the MG-$Mg_{1.9}Al_{0.1}Ni$ system.

3.3. Hydrogen storage properties of Mg_2Ni alloy mechanically ground with Pd

As described above, Ni particles dispersed in the Mg_2Ni alloy obviously play an important role in increasing the electrode capacity at room temperature. On the other hand, it was reported that the electrocatalytic activity of the modified hydrogen storage alloy electrodes due to electrodeposition of foreign metals increased in the order of Fe<Ni<Co<Pd [12]. Zaluski et al. [15] also reported that the hydrogen storage alloy powders modified with Pd readily absorb hydrogen gas at room temperature with no activation applied. Therefore, hydrogen storage properties of Mg_2Ni ground mechanically with Pd were investigated.

Fig. 6 shows the XRD pattern of MG-(Mg_2Ni+Pd). It was found that the characteristic peaks of the Mg_2Ni phase also decreased in intensity and broadened. MG-(Mg_2Ni+Pd) alloy was transformed to an amorphous-like state. The existence of the large diffraction peaks attributed to the Pd metal suggested that the Pd still remains in its crystal state.

Fig. 7 shows that the discharge capacity of MG-(Mg_2Ni+Pd) alloy electrode had a discharge capacity of 420 mAh/g at the 20th cycle, though this alloy electrode had a discharge capacity of 600 mAh/g at the first cycle. These results suggested that nickel might not be essential in improving hydrogen storage properties. The element such as Pd, which has a large catalytic activity for hydrogen electrode reaction, is a suitable additive for this MG treatment. The nano-size Pd particles dispersed in the Mg_2Ni alloy may also work as a catalytic site for hydrogen absorption reaction, and improve the hydrogen storage properties.

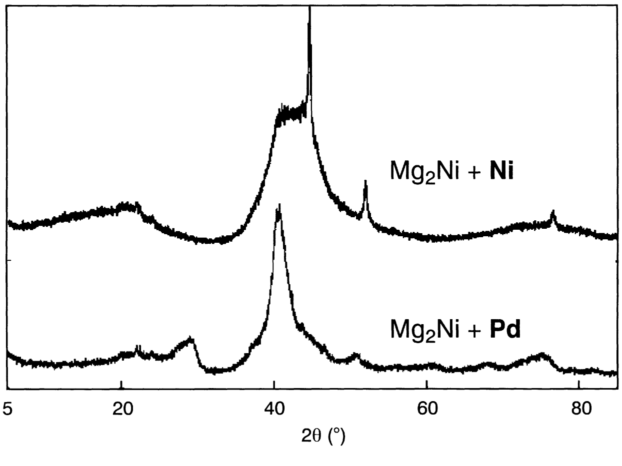

Fig. 6. XRD patterns of MG-(Mg_2Ni+Ni) and MG-(Mg_2Ni+Pd).

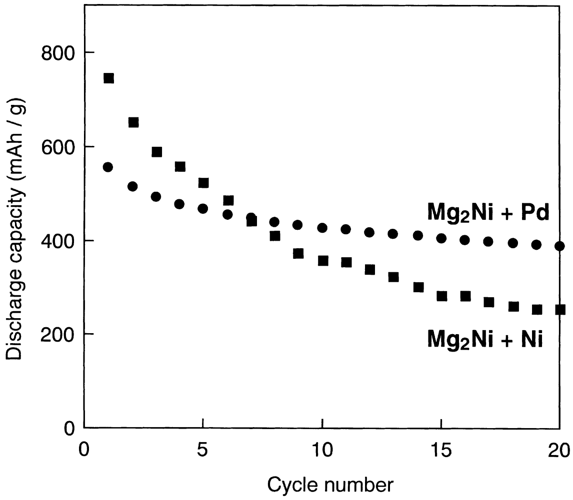

Fig. 7. Discharge capacities of MG-(Mg_2Ni+Ni) and MG-(Mg_2Ni+Pd).

4. Summary

MG-Mg_2Ni system alloy electrode shows notably increased capacity up to 830 mAh/g in alkaline solution at room temperature, compared with that of Mg_2Ni. The additional Ni may work as a catalytic site for the hydrogen dissociation surface, and improve the hydrogen storage properties. Consequently, it becomes possible for the MG-Mg_2Ni system alloy electrode to discharge at room temperature. The partial substitution of Mg with Al, B, C and Ag improved the reversibility. In particular, in the MG-$Mg_{1.9}Al_{0.1}Ni$ system, the cycle life was considerably improved without losing much initial capacity. The element such as Pd, which has a high catalytic activity of hydrogen electrode reaction, was also suitable as the additive of this MG treatment, because the kinetics of the hydrogen electrode reaction was remarkably increased. These nano-size Pd particles may also work as a catalytic site, and improve the hydrogen reversibility of this alloy. These results suggest the possibility of realizing a lightweight battery with higher capacity than those employing alloys commonly adopted at present.

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