Effects of Carbon Crystallinity on Hydriding-Dehydriding and Charge-Discharge Characteristics of MgNi Alloy-Carbon Material Composites

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Hydriding-dehydriding and charge-discharge characteristics of amorphous MgNi alloys modified by ball-milling with different carbon materials were investigated with the intention of using them in nickel-metal hydride batteries. It was found that the ball-milling with carbon materials markedly improved hydriding-dehydriding and charge-discharge characteristics of the MgNi alloy, and an optimum ball-milling time was shortened by utilization of carbon material with lower crystallinity. However, ball-milling for longer than the optimum time led to a decrease in the amount of absorbed hydrogen and the discharge capacity, which was ascribed to the formation of MgNi₃C. These results indicate that the characteristics of MgNi alloy-carbon material composites greatly depend on both crystallinity of carbon material used and ball-milling time.

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1. Introduction

Mg-based hydrogen storage alloys are very attractive materials for energy conversion and storage, but high temperature is generally required for their reversible absorption and desorption of hydrogen. Recently, many efforts have been made to improve their hydriding-dehydriding and charge-discharge characteristics at relatively low temperature from a practical point of view. Our group first reported that a crystalline Mg₂Ni alloy prepared by induction melting could absorb and desorb hydrogen electrochemically at 70°C and exhibited a maximum discharge capacity, ca. 400 mAh g⁻¹, in a 6M KOH solution. Lei et al. first and our group later reported that an amorphous MgNi alloy prepared by mechanical alloying (MA) exhibited a very high discharge capacity even at room temperature. These presented a new possibility for the application of Mg-based alloys in nickel-metal hydride batteries. Moreover, it was reported that preparation of Mg₂Ni alloys with a nanocrystalline or amorphous structure by ball-milling led to the improvement in the hydriding-dehydriding and/or charge-discharge characteristics. In order to improve hydriding-dehydriding and charge-discharge characteristics of Mg-based alloys further, surface modifications by ball-milling with other materials have been carried out. In our previous papers, it was found that surface modification by ball-milling of the Mg-based alloys with graphite markedly increased the rate of hydrogen absorption and improved the charge-discharge characteristics. It was also reported that an interaction between the MgNi alloy surface and ball-milled graphite with a low crystallinity appeared by ball-milling, leading to an increase in Ni/Mg ratio on the alloy surface. The crystallinity of graphite or other carbon materials may be an important factor for determining the hydriding-dehydriding and charge-discharge characteristics. Therefore, in this study, surface modification of the amorphous MgNi alloys was carried out using carbon materials with different crystallinities, and hydriding-dehydriding and charge-discharge characteristics of the MgNi alloy-carbon material composites were investigated.

2. Experimental

MgNi alloy was prepared from Mg and Ni mixed powders (total mass of 1 g) by MA under Ar atmosphere using a planetary mill with an acceleration of ca. 30 m s⁻² for 36 h. Three carbon materials with different crystallinity, graphite (synthetic graphite, Nippon Graphite Industries, SP-10), MCMB1800°C (mesocarbon microbeads, Osaka Gas) and Ketjen black (carbon black, Ketjen Black International Company), were used for surface modification of the MgNi alloy. X-ray diffraction (XRD) patterns of these carbon materials are shown in Fig. 1. The order of crystallinity is as follows: graphite > MCMB1800°C > Ketjen black. The resulting MgNi alloy powders were mixed with the carbon material powders (mass ratio to alloy: 0.2) and then ball-milled with an acceleration of ca. 100 m s⁻² for different periods to

![Fig. 1 X-ray diffraction patterns of graphite, MCMB1800°C and Ketjen black.](image-url)
Hydriding characteristics were measured in hydrogen gas of 3 MPa at 30°C using a Sieverts' apparatus in the same manner as described in our previous papers. Hydriding rate, \( d(H/M)/dt \), when the amount of absorbed hydrogen reached half of the saturated one was defined as \( v_{1/2} \). Thermodgravimetry (TG) for the samples sufficiently hydrided in hydrogen gas of 3 MPa at 30°C for 24 h was carried out under Ar flow with the heating rate of 10°C min\(^{-1}\). On the basis of the TG data, dehydriding characteristics were evaluated. Experimental details including the preparation of negative electrodes and charge-discharge cycling tests, and apparatus used in this work were the same as those described in our previous papers. Each negative electrode was charged at 100 mA g\(^{-1}\) for 6 h and discharged to \(-0.6\) V vs. Hg/HgO at 50 mA g\(^{-1}\) in (6 kmol m\(^{-3}\) KOH + 1 kmol m\(^{-3}\) LiOH) solution at 30°C. After every charging, the circuit was opened for 10 min. Discharge capacity was calculated based on the mass of MgNi alloy.

3. Results and Discussion

Figure 2 shows XRD patterns for MgNi alloy and MgNi alloy-carbon material composites prepared by ball-milling for 10 min. In our previous paper, the ball-milling time of 10 min was found to be optimum for the MgNi alloy-graphite composite. As can be seen from Fig. 2, a broad diffraction peak was observed for the MgNi alloy, indicating that the MgNi alloy prepared by MA had an amorphous structure. This was confirmed from TEM image and electron diffraction pattern in our previous paper. For the MgNi alloy-graphite composite, diffraction peaks except for those due to the MgNi alloy and ball-milled graphite were not observed under this condition. On the other hand, peaks due to MgNi\(_2\)C\(^{16}\) were clearly observed for MgNi alloy-MCMB1800°C and MgNi alloy-Ketjen black composites. This suggests that MgNi\(_2\)C is formed more easily by using carbon material with lower crystallinity.

Hydriding characteristics of MgNi alloy and MgNi alloy-carbon material composites prepared by ball-milling for 10 min were shown in Fig. 3. Hydriding rate of the MgNi alloy was very low and the amount of absorbed hydrogen finally reached a saturated H/M value of ca. 1.03 after ca. 10 h.\(^{11}\) As can be seen from this figure, ball-milling with carbon materials markedly increased the hydriding rate of the MgNi alloy. Moreover, it was found that the hydriding rate was larger with lowering the crystallinity of carbon material used. Hydriding rates, \( v_{1/2} \) s, for the cases of Ketjen black, MCMB1800°C and graphite were ca. \(7.4 \times 10^{-3}\) s\(^{-1}\), ca. 3.9 \(\times 10^{-3}\) s\(^{-1}\) and ca. 1.2 \(\times 10^{-3}\) s\(^{-1}\), respectively. On the other hand, lowering the crystallinity of carbon material used led to a decrease in the saturated amount of absorbed hydrogen. It is suggested from XRD patterns in Fig. 2 that the decrease in the saturated amount of absorbed hydrogen may be due to the formation of MgNi\(_3\)C. Supposing that all of the absorbed hydrogen were electrochemically desorbed, discharge capacities calculated from the saturated amounts of absorbed hydrogen (H/M = ca. 1.07 and ca. 0.76) for MgNi alloy-graphite and MgNi alloy-Ketjen black composites could be ca. 690 mAh g\(^{-1}\) and ca. 490 mAh g\(^{-1}\), respectively. A decrease in the saturated amount of absorbed hydrogen would lead to a decrease in the discharge capacity.

In order to clarify the reason of the low saturated amount of absorbed hydrogen for MgNi alloy-Ketjen black composite, effects of ball-milling time on hydriding characteristics of the composite were investigated. Figure 4 shows time course of the amount of absorbed hydrogen for MgNi alloy-Ketjen black composite ball-milled for 2 min. Although the hydriding rate (\(v_{1/2} = ca. 1.4 \times 10^{-3}\) s\(^{-1}\)) is relatively low compared with the case of 10 min in Fig. 3, the saturated amount of absorbed hydrogen markedly increased to a similar value to that for MgNi alloy-graphite composite ball-milled for 10 min. It was suggested that the formation of MgNi\(_2\)C was suppressed by ball-milling for shorter time, leading to suppression of a decrease in the saturated amount of absorbed hydrogen for the MgNi alloy. Therefore, MgNi alloy-Ketjen black composite ball-milled for 2 min is expected to show a large discharge capacity as well as MgNi alloy-graphite composite ball-milled for 10 min. In addition, the relatively low hydriding rate of MgNi alloy-Ketjen black composite ball-milled for 2 min compared with the case of 10 min indicates that catalytic activity for hydrogen absorption was improved during ball-milling between 2 and 10 min, while the formation of the
MgNi$_3$C simultaneously occurred.  

Figure 5 shows TG curves of hydrided MgNi alloy and MgNi alloy-carbon material composites. In this figure, a weight loss and a slight weight gain in high temperature region for each TG curve are due to hydrogen desorption of the hydrided sample and oxidation of the alloy surface by residual oxygen, respectively. As can be seen from this figure, dehydriding temperature was markedly lowered by the modification with carbon materials. This indicates that carbon materials are very effective in improving not only hydriding but also dehydriding characteristics of the MgNi alloy. In the case of ball-milling time of 10 min, the amount of desorbed hydrogen for the MgNi alloy-Ketjen black composite was lower than that for the MgNi alloy-graphite composite, due to the lower saturated amount of absorbed hydrogen. However, by shortening the ball-milling time to 2 min, the MgNi alloy-Ketjen black composite showed similar dehydriding behavior to that for the MgNi alloy-graphite composite ball-milled for 10 min.  

Charge-discharge cycle tests were carried out at 30°C to investigate the electrochemical characteristics of MgNi alloy-carbon material composites. Discharge curves (1st cycle) for MgNi alloy-graphite and MgNi alloy-Ketjen black composites ball-milled for 10 and 2 min, respectively, are shown in Fig. 6, compared to that for MgNi alloy. For each case, a plateau of the potential caused by the oxidation of absorbed hydrogen was observed. Although the plateau potential was hardly changed by the modification with carbon material, the discharge capacity was markedly increased. The similar result was previously observed for the MgNi alloy and MgNi alloy-graphite composite in a different condition.  

Figure 7 shows discharge capacities (1st cycle) as a function of ball-milling time for MgNi alloy-carbon material composites. Samples ball-milled for 0 min mean mixtures of the MgNi alloy and carbon materials without ball-milling. As can be seen from this figure, the ball-milling time to reach the value was shortened by utilization of carbon material with lower crystallinity. Moreover, in any cases, ball-milling for longer than the optimum time led to a decrease in the discharge capacity. It can be inferred that the reason of the decrease in the discharge capacity as well as the saturated amount of absorbed hydrogen may be mainly attributed to the formation of MgNi$_3$C.  

In order to investigate the reason of the decreases in the saturated amount of absorbed hydrogen and the discharge capacity in detail, XRD analyses were carried out for MgNi
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Fig. 8 X-ray diffraction patterns of (a) MgNi alloy-graphite and (b) MgNi alloy-Ketjen black composites prepared by ball-milling for different times.

Fig. 9 Discharge capacities (30°C) as a function of cycle number for MgNi alloy, MgNi alloy-graphite (ball-milling time: 10 min) and MgNi alloy-Ketjen black (ball-milling time: 2 min) composites.

...alloy-carbon material composites ball-milled for different times. XRD patterns for MgNi alloy-graphite and MgNi alloy-Ketjen black composites are shown in Fig. 8. Visible peaks due to MgNi$_3$C were hardly observed in the cases of 10 and 2 min or shorter ball-milling time for MgNi alloy-graphite and MgNi alloy-Ketjen black composites, respectively. However, the peaks due to MgNi$_3$C were clearly observed for the composites ball-milled for longer than the optimum time. It was also confirmed that MgNi$_3$C hardly absorb hydrogen by measurements of both hydriding-dehydriding and charge-discharge characteristics. These results indicate that the formation of MgNi$_3$C cause a decrease in the saturated amount of absorbed hydrogen of the MgNi alloy, leading to a decrease in the discharge capacity. Furthermore, it was clarified that MgNi$_3$C formed more easily by using carbon material with lower crystallinity.

Figure 9 shows discharge capacities as a function of cycle number for MgNi alloy, MgNi alloy-graphite and MgNi alloy-Ketjen black composites ball-milled for 10 and 2 min, respectively. The discharge capacity of the MgNi alloy decreased seriously with increasing cycle number. This can be ascribed to the formation of Mg(OH)$_2$ on the alloy surface in alkaline solution during charge-discharge cycling. As can be seen from this figure, surface modification with carbon material markedly improved the cycle performance. It is suggested that the modification suppressed the formation of Mg(OH)$_2$ on the alloy surface and kept the high saturated amount of absorbed hydrogen and high electrocatalytic activity even with increasing cycle number. Under the present condition, the MgNi alloy-Ketjen black composite exhibited better cycle performance than the MgNi alloy-graphite composite. Utilization of Ketjen black with high specific surface area may be more effective in suppressing the oxidation compared with the case of graphite. All results as mentioned above indicate that hydriding-dehydriding and charge-discharge characteristics of MgNi alloy-carbon material composites greatly depend on the crystallinity of carbon material used and that optimum characteristics can be obtained by controlling ball-milling time.

In our previous paper, it was strongly suggested that the charge-transfer reaction occurred between Mg and graphite by ball-milling MgNi alloy together with graphite, resulting in an increase in Ni/Mg ratio on the alloy surface. Imamura et al. also reported that charge-transfer complexes formed between Mg or Mg$_2$Ni alloys and various aromatic molecule and this kind of complexes had high catalytic activity for hydrogen activation, which was confirmed by H$_2$-D$_2$ isotope scrambling measurements. Moreover, metallic Ni is well-known to have high catalytic activity for hydrogen absorption and desorption. Therefore, enhanced hydriding-dehydriding characteristics for MgNi alloy-Ketjen black and MgNi alloy-MCMB1800°C composites can be also ascribed to the formation of charge-transfer complexes between Mg and carbon material and an increase in the Ni/Mg ratio on the alloy surface. As for electrochemical reactions, it is well-known that Ni-rich surface layer gives high electrocatalytic activity and good conductivity to the alloy surface. In addition, the formed charge-transfer complexes may work as better electrocatalysts than Mg or Mg(OH)$_2$ formed on the alloy surface in alkaline solution. Moreover, Ni-rich surface layer and the charge-transfer complexes may have better corrosion resistance than the unmodified alloy surface. It can be inferred that these effects lead to the large discharge capacity and relatively good cycle performance. Even in the case of utilization of carbon material with lower crystallinity such as Ketjen black and MCMB1800°C, a microstructural change could be explained with the same mechanism as proposed for MgNi alloy-graphite composites in the previous paper. It is suggested that the carbon material with lower crystallinity interacts more easily with the MgNi alloy surface, leading to the formation of charge-transfer complexes and an increase in the Ni/Mg ratio with shorter ball-milling time. Along this line, more detailed investigation is now in progress.
4. Conclusion

For MgNi alloy-carbon material composites prepared by ball-milling for 10 min, the rate of hydrogen absorption was increased by using carbon material with lower crystallinity. However, the saturated amount of absorbed hydrogen was lowered, which is ascribed to the formation of MgNi$_3$C in the composites. MgNi alloy-Ketjen black composite ball-milled for 2 min showed enhanced hydriding-dehydriding characteristics similar to those for MgNi alloy-graphite composite ball-milled for 10 min. Moreover, the ball-milling time to reach the maximum discharge capacity was shortened by utilization of carbon material with lower crystallinity. It can be inferred that carbon material with lower crystallinity may interact more easily with the MgNi alloy surface, leading to optimum hydriding-dehydriding and charge-discharge characteristics with shorter ball-milling time.

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