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Discharge Capacities of $Mg_{1-x}Nd_xNi$ (x = 0, 0.05, 0.1, 0.2) Alloys Prepared by Mechanical Alloying

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In this study, the $Mg_{1-x}Nd_xNi$ (x = 0, 0.05, 0.1, and 0.2) alloys were prepared by mechanical alloying (MA), and their electrochemical properties were measured by simulated battery test. It is observed that the introduction of Nd can accelerate the formation of the amorphous structure of MgNi alloy. With the increasing milling time from 40 to 60 h, the initial discharge capacity of $Mg_{1-x}Nd_xNi$ (x = 0, 0.05, 0.10, and 0.20) alloys increases gradually, while during the milling time from 60 to 70 h, it decreases. The maximum capacity of the $Mg_{1-x}Nd_xNi$ alloys is gradually reduced with increasing Nd content x. With the milling time t = 60 h and x = 0, the discharge capacity is increased up to 378.2 mAh/g. Experimental results show that partial substitution of Mg with Nd can improve cyclic stability of the amorphous MgNi sample at the expense of a reduction in the initial capacity.

Keywords electrochemical properties, mechanical alloying, the amorphous MgNi alloy

1. Introduction

Magnesium-based alloys are promising hydrogen storage materials because Mg has advantageous characters including safety, atmospheric stability, lower cost compared to other series of hydrogen storage materials, and high natural abundance. However, the practical application of Mg-based alloys is restrained by their poor hydriding-dehydriding kinetics at room temperature and their poor charge-discharge cycle stability (Ref 1). In the past few years, researchers have been making efforts to increase the rates of hydrogen absorption and desorption at lower temperature (Ref 2, 3). The Mg-Ni-Nd alloys have been investigated for many years to study the effect of the introduction of Nd on electrochemical characteristics of Mg_2Ni alloy (Ref 4-8). Although the mechanism of degradation for amorphous MgNi alloys and the methods to improve cyclic stability have been widely studied at present (Ref 9-13), no study has so far reported that the rare earth Nd affects the electrode property of MgNi amorphous alloy.

In this study, in order to avoid the significant degradation of the cyclic stability, the partial Mg of MgNi alloy prepared by mechanical alloying is substituted by Nd which acts as an efficient catalyst. Their corresponding structural characteristics, discharge capacity, and cyclic stabilities are investigated in detail.

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2. Experimental

$Mg_{1-x}Nd_xNi$ (x = 0, 0.05, 0.1, and 0.2) ternary alloys were synthesized by mechanical alloying (MA). Elemental powders with sizes of 100-150 mesh and purity higher than 99.9% were used. The milling process was performed under the protection of pure argon in a QM-1SP4 planetary ball mill at 400 rpm for 40, 50, 60, and 70 h, respectively. The weight ratio of steel ball to powder was 25:1. The milled specimens were checked by x-ray diffraction with Cu Kα radiation (λ = 0.1541 nm) to obtain information about the phase composition and the crystallinity.

The $Mg_{1-x}Nd_xNi$ (x = 0, 0.05, 0.1, 0.2) alloy electrodes were prepared by the following procedures: First, approximately 0.2 g of the MA alloy was mixed uniformly with electrolyte Cu powder (about 250 mesh) in a mass ratio 1:2, and then fixed with Teflon (PTFE) onto a foam Ni holder (3.5 cm × 3.5 cm). Subsequently, the foam nickel pasted with alloy powder was pressed at 150 kgf/cm^2 after drying. Finally, the prepared electrode was electrochemically charged and discharged in 6 M KOH electrolyte in an electrochemical cell open to the atmosphere. The test electrode properties were measured at 298 K using a battery test apparatus (PCBT-138-8D-A). In the charge-discharge measurement, negative electrodes were charged at 150 mA/g for 3 h and discharged to 0.9 V at 100 mA/g.

3. Results and Discussion

3.1 Structural Characteristics

Figure 1 shows the XRD patterns of the $Mg_{1-x}Nd_xNi$ (x = 0, 0.05, 0.1, and 0.2) alloys after mechanical alloying for 40 h (A), 50 h (B), 60 h (C), and 70 h (D) at 400 rpm, respectively. All the alloys exhibit similar broad diffuse peaks at 38-47°, namely, the featureless appearance is typical for an amorphous structure. This implies that the partial replacement of Mg by Nd does not change the major amorphous phase structure of MgNi. At the same time, these data also indicate a trend of changing toward sharper diffraction peaks with increasing milling time. With increasing x, their intensities decrease, and the maximum positions of the halos shift to slightly higher angles, which implies more uniformity of elements in the amorphous structure. It also suggests that the average interatomic distances in the amorphous phase are reduced with the increase of Nd content.

In Fig. 1(A), a diffracted intensity of the (111) plane of Ni at about 45° can be observed weakly in the x-ray diffraction pattern of MgNi sample milled for 40 h, which means that this sample is not fully amorphous. With higher milling times, the signal of the (111) plane of Ni disappears gradually as well as with increasing Nd content x. In Fig.1(D), we also observe a little sharp diffraction peak in XRD pattern of $Mg_{0.8}Nd_{0.2}Ni$ sample, which implies that the transformation of amorphous into crystallization has started in this alloy. Based on the results discussed above, it is concluded that the introduction of Nd can accelerate the formation of the amorphous structure of MgNi alloy.

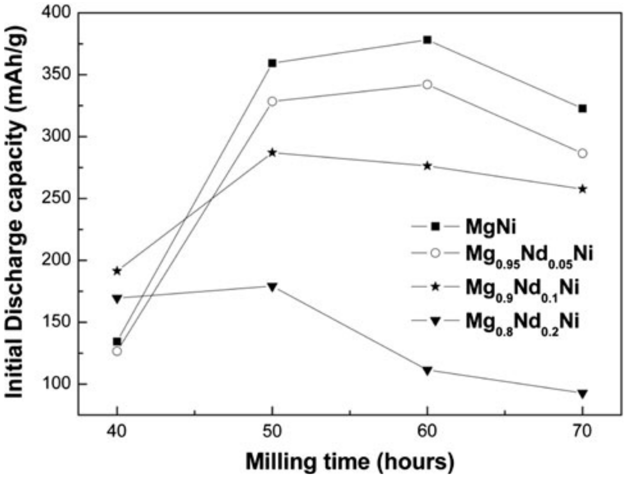

Fig. 2 Variations in the initial discharge capacity vs. the milling time for the $Mg_{1-x}Nd_xNi$ (x = 0, 0.05, 0.1, 0.2) samples

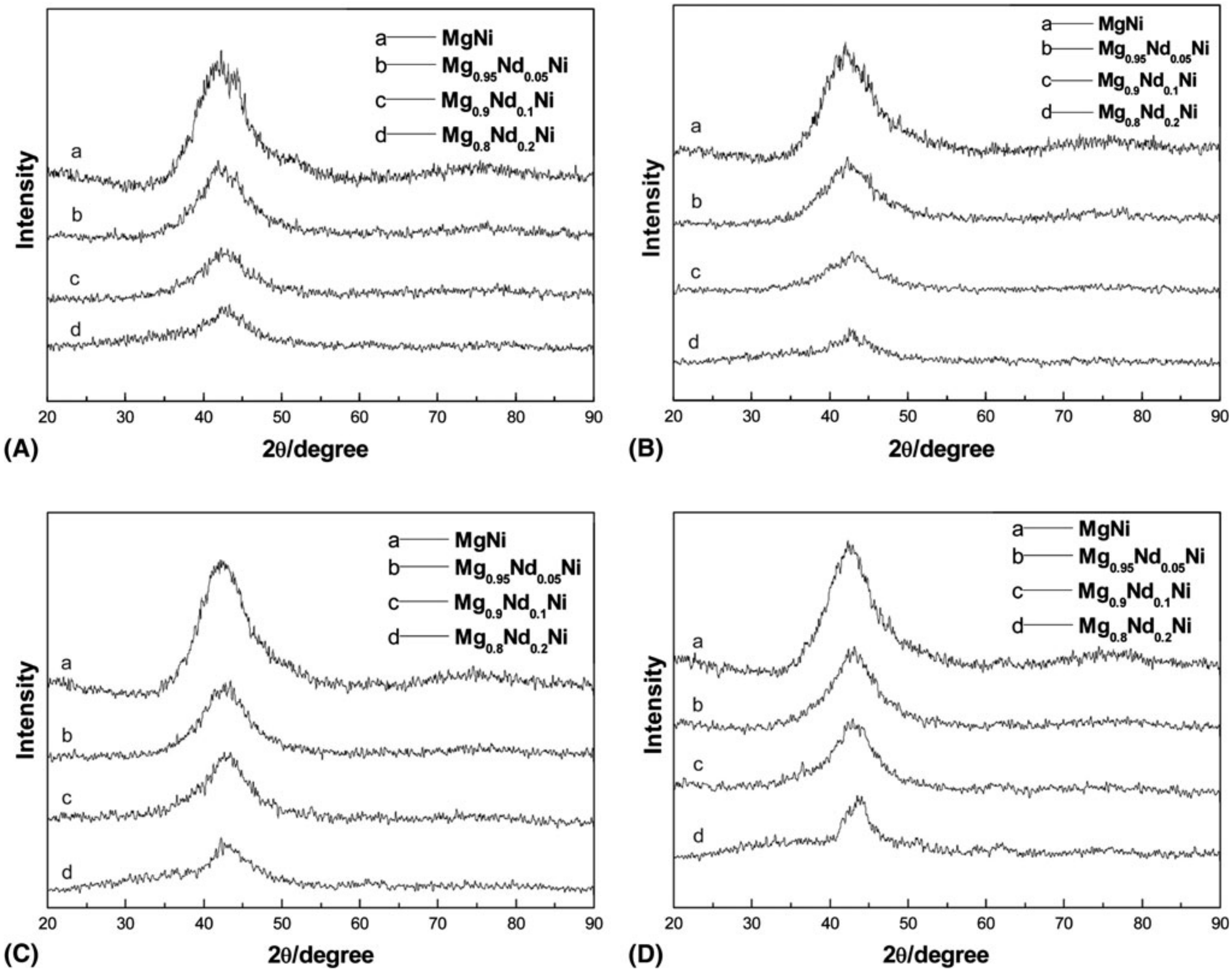

Fig. 1 The XRD patterns of the $Mg_{1-x}Nd_xNi$ (a, x = 0; b, x = 0.05; c, x = 0.1; d, x = 0.2) alloys milled at 400 rpm for 40 h (A), 50 h (B), 60 h (C), and 70 h (D), respectively

3.2 Initial Discharge Capacity

The effects of mechanical alloying time on the initial discharge capacity of $Mg_{1-x}Nd_xNi$ ($x = 0$, 0.05, 0.1, and 0.2) alloys are presented in Fig. 2. As the mechanical alloying time increases, the initial discharge capacity increases gradually and achieves the maximum at 60 h, then decreases, which may be related with their grain size. At the same time, it is found that the maximum discharge capacities of both MgNi alloy when milled for 40 h and $Mg_{0.8}Nd_{0.2}Ni$ alloy when milled for 70 h are the lowest. Together with the results of x-ray diffraction, it indicates that the crystallization may be responsible for the decay of the discharge capacity.

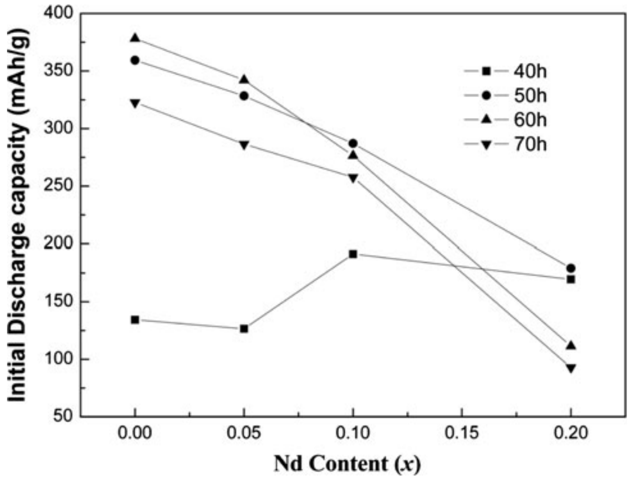

Fig. 3 Relationship of the initial discharge capacity and the Nd content x for the $Mg_{1-x}Nd_xNi$ samples

The dependence of the initial discharge capacity of the $Mg_{1-x}Nd_xNi$ ($x = 0$, 0.05, 0.1, and 0.2) alloys on Nd content x is shown in Fig. 3. It is found that the initial discharge capacity of the $Mg_{1-x}Nd_xNi$ alloys is gradually reduced with increasing Nd content x. With the milling time $t = 60$ h and $x = 0$, the discharge capacity increases up to 378.2 mAh/g. These phenomena may be because lower Mg content leads to a lower H-capacity.

3.3 Cyclic Stability

The changes of the electrochemical discharge capacities of amorphous $Mg_{1-x}Nd_xNi$ ($x = 0$, 0.05, 0.10, and 0.20) alloys of electrodes with increase in the number of cycles are shown in Fig. 4. It is clearly seen that all the discharge capacities of $Mg_{1-x}Nd_xNi$ ($x = 0$, 0.05, 0.1, and 0.2) alloys become decreased during the cycling tests. In the case of the MgNi

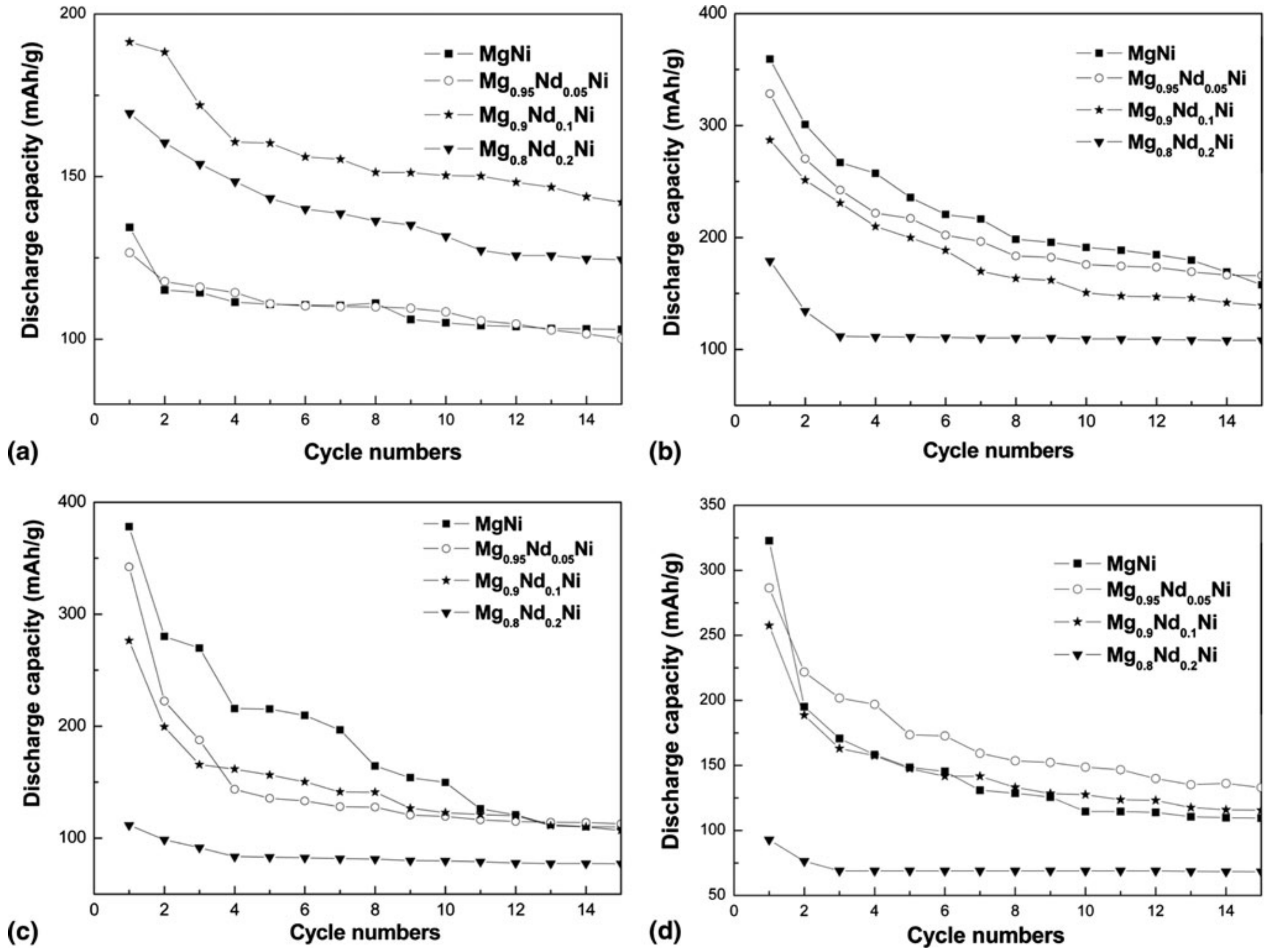

Fig. 4 Electrochemical discharge capacities as a function of the cycle number for $Mg_{1-x}Nd_xNi$ ($x = 0$, 0.05, 0.1, 0.2) alloys milled at 400 rpm for 40 h (a), 50 h (b), 60 h (c), and 70 h (d), respectively

electrode, the discharge capacity gets decreased dramatically with increasing cycle number. This is caused by selective magnesium oxidation in the highly corrosive 6 M KOH electrolyte. Hence, the cycle life of the binary MgNi alloy electrode is very poor, which is a strong barrier to its practical application. Therefore, in order to improve the cycle life of the amorphous Mg-based alloys, a suppression of the oxidation of the alloys is necessary.

On the other hand, the decrease in the discharge capacity for the $Mg_{1-x}Nd_xNi$ ($x = 0.05$, 0.1, and 0.2) electrodes are slower than that for the MgNi electrode, particularly the curve of the discharge capacity for $Mg_{0.8}Nd_{0.2}Ni$ sample turns to smooth after three cycles, although it has the lowest capacity. This may be because Nd is introduced to suppress the formation of a thick oxide layer through continuous oxidation, as well as cause a refined microstructure and simultaneously provide catalytic surface structures. Spassov et al. (Ref 14) observed an improvement in the hydrogenation kinetics of $Mg_{63}Ni_{30}Y_7$ alloy due to the catalytic effect of yttrium. The remaining Ni may be also resistant to oxidation. Although the partial replacement of Mg by Nd improves the cycle life of the MgNi alloys, they are at the expense of a reduction in the initial capacity. This may be due to the lower Mg content of alloys, because Mg is a main absorbing element.

4. Conclusion

All $Mg_{1-x}Nd_xNi$ ($x = 0$, 0.05, 0.1, and 0.2) alloys were prepared by mechanical alloying. The results obtained are summarized as follows:

(1) The introduction of Nd can accelerate the formation of the amorphous structure of MgNi alloy.
(2) With the increasing milling time from 40 to 60 h, the initial discharge capacities of $Mg_{1-x}Nd_xNi$ ($x = 0$, 0.05, 0.10, and 0.20) alloys increases gradually while from 60 to 70 h, it decreases. The maximum capacity of the $Mg_{1-x}Nd_xNi$ alloys is gradually reduced with increasing Nd content x. With the milling time $t = 60$ h and $x = 0$, the discharge capacity increases up to 378.2 mAh/g.
(3) The initial capacity of the amorphous MgNi sample is reduced by partial substitution of Mg with Nd, but its cyclic stability can be improved.

From above results, it is concluded that the Nd addition is more effective in terms of the improvement in the cyclic stability except for the reduction in the initial discharge capacity for MgNi amorphous alloy. For the practical use of MgNi alloy which has large electrochemical discharge capacity, it is significant that the life cycle property be improved, while retaining the maximum discharge capacity. Therefore, further studies will be needed to optimize the Nd composition.

Acknowledgments

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