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The Electrode Properties of $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ Alloy by Mechanical Grinding with Ni Powders

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A modified magnesium alloy of composition $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ was prepared by mechanical grinding with Ni powder for periods up to 120 h. The resulting structures of the $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloys were found to be amorphous. The electrodes of the modified $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloys had large discharge capacities. At a discharge current rate of 50 mA/g, the capacity was 630 mAh/g after 50 h of mechanical grinding and 510 mAh/g after 120 h of mechanical grinding.

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Magnesium-based hydrogen storage alloys possess very high hydrogen absorption capacity (e.g., Mg_2NiH_4 contains 3.6 wt % of hydrogen). Magnesium is also abundant in nature, light in weight, and low in cost. As a result, magnesium alloys have become the subject of increasing research worldwide. For a long period, it was thought that Mg-based alloy-hydrogen systems needed to be operated at a high temperature (over 250°C) and under high hydrogen pressure. However, in recent years, some research work was done to improve the hydrogen absorption kinetics of Mg_2Ni by mechanical grinding and alloying. Some nano- and amorphous-structured Mg_2Ni alloys could absorb hydrogen even at room temperature. Nohara et al.¹ reported that the Mg-based alloy prepared by mechanical alloying can absorb hydrogen at 30°C in much larger quantities than that prepared by induction melting. Zaluski et al.² reported that nanocrystalline Mg_2Ni alloy modified with Pd by milling absorbs hydrogen at room temperature without activation. These examples show that it is possible to use Mg_2Ni -type alloys as promising materials for increasing the negative electrode capacity of Ni-metal hydride(MH) batteries because 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).

Recently, Lei et al. obtained improved discharge capacity for Mg-based alloys prepared by mechanical alloying (MA).^{3,4} Iwakura et al.⁵ have also improved the discharge capacity of MA Mg-based alloy with graphite surface modification by ballmilling.

After surface modification with Ni powder by ballmilling, Kohno et al. have obtained large discharge capacity for modified Mg_2Ni alloys.^{6,7} In our research work, we made a $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloy modified by Ni powder using mechanical grinding (MG) and measured its discharge capacity as a negative electrode compared with its crystalline counterpart alloy.

Experimental

The $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloy (MNA) was prepared by sintering the pure Mg, Ni, Al, Co, and Mn powders in their required proportions under an argon atmosphere at 700°C for 9 h. To ensure that the target compositions were not significantly changed in our experiments, we pressed the metal powders with a very high pressure and used a sealed stainless steel tube furnace under a high pressure of argon gas (ca. 2 atm). We also used a very slow heating rate to reach 700°C. In the slow heating process, the Mg powders would combine with Ni powders to form the Mg_2Ni phase gradually before the temperature reached the melting point of Mg. Mechanical grinding was performed with a Fritsch planetary ball mill. The vial and balls are made from stainless steel and hardened steel, respectively. Then, 1 mol of MNA alloy and 3 mol pure Ni were mixed and milled at 150 rpm in an argon atmosphere. The weight ratios of ball to sample were 30:1. After each specified number of hour of milling, the milled powders were examined by X-ray diffraction (XRD).

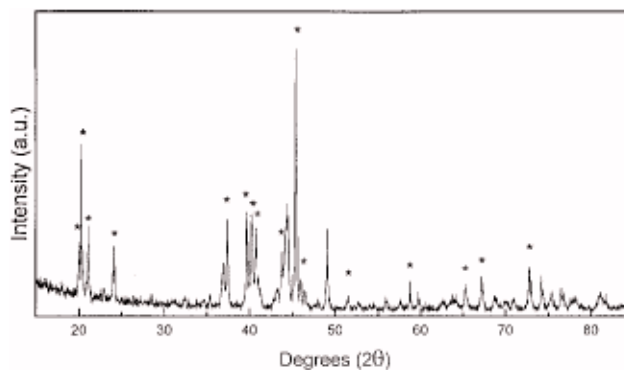


Figure 1. The X-ray pattern of the sintered $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloy. (* : Mg_2Ni phase.)

XRD was conducted using a Philips PW1010 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Morphologies of the powders of MNA alloys were observed through a Leica Stereoscan 440 scanning electron microscope (SEM).

The sintered MNA alloy was crushed into powder and mixed with Ni powder in the weight ratio of 1:2 to make an electrode. The hydrogen storage alloy powders obtained from MG with 50 h (MNA-50) and 120 h (MNA-120) were also mixed with Ni powder in the weight ratio of 1:1 for making an electrode. The hydride electrodes were fabricated by mixing the resultant powders with polyvinyl alcohol solution and pasting them into a foamed nickel matrix which acted as the current collector for the electrode. The hydride electrodes were then compressed at a load of 40 MPa for 1 min. The hydride 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 MNA alloys were measured using a DC-5 battery test instrument. In the charge-discharge cycle tests, the charge cycle was initiated using a current density of 100 mA per gram of hydrogen storage alloy for 10 h, then after a 1 min 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. After the first charge-discharge cycle test, the charge capacity was about 1.3 times its previous discharge capacity.

Results and Discussion

Our reasons for choosing Co, Mn, and Al additions resulted from some published papers which show that Co and Mn elements can increase the cycle life of MgNi amorphous alloy,^{4,8} and also that Al can increase the cycle life of a Mg_2Ni -Ni amorphous alloy.⁷ However, there has been no previous study of the combined efforts of all three elements on the electrode properties.

The X-ray pattern of the sintered MNA alloy is shown in Fig. 1. The main phase of the sintered Mg, Ni, Al, Co, and Mn powders after sintering for 9 h at 700°C is still the Mg_2Ni phase with a crys-

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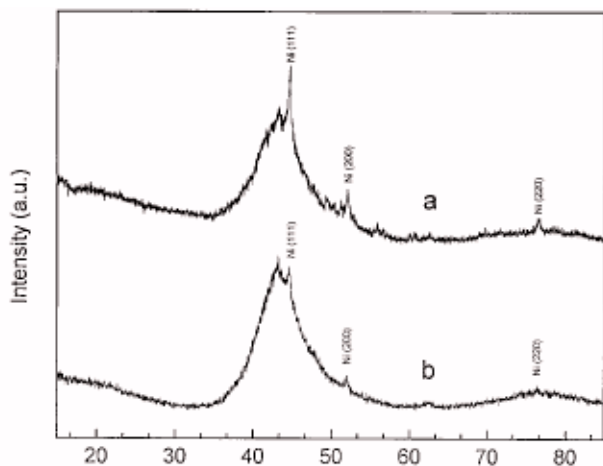


Figure 2. The X-ray pattern of $Mg_{1.9}Al_{0.1}Ni_{0.8}Co_{0.1}Mn_{0.1}$ alloy mechanically ground with Ni powders after grinding for (a) 50 and (b) 120 h.

talline structure. Identification of the Al, Co, and Mn elements is not clear because of their relatively small content. Figure 2 shows the X-ray pattern of the MNA alloys mechanical ground with Ni powders in the molar ratio of 1:3 after grinding for 50 and 120 h. Note that the structure of the MNA alloy has been greatly changed. After grinding for 50 h, the microstructure of the MNA-50 alloy seems to be amorphous while the Ni is still crystalline. However, after grinding for 120 h, the microstructure of the MNA-120 alloy is still amorphous, but the Ni peak decreases. The X-ray results of the MNA-50 and MNA-120 alloys are consistent with the results of previous work on the MG-Mg₂Ni after grinding for 100 h.^{6,7}

Figure 3a, b, and c show the images of the MNA-50 alloy and Fig. 3d, e, and f show the images of the MNA-120 alloy. The MNA-50 and MNA-120 alloys have similar particle sizes, in the range of ~1-12 μm (Fig. 3a and d). The particles of the MNA-50 alloy consist of visibly separated layers of the MNA alloy and nickel (Fig. 3a, b, and c). However, the particles of the MNA-120 alloy have more uniform and smoother surfaces which are consistent with the formation of amorphous Ni and MgNi.⁹ The particles shown in Fig. 3d, e, and f also appear to be brighter than those in Fig. 3a, b, and c. This means that the MNA-120 alloy has probably more Ni atoms on the surface.

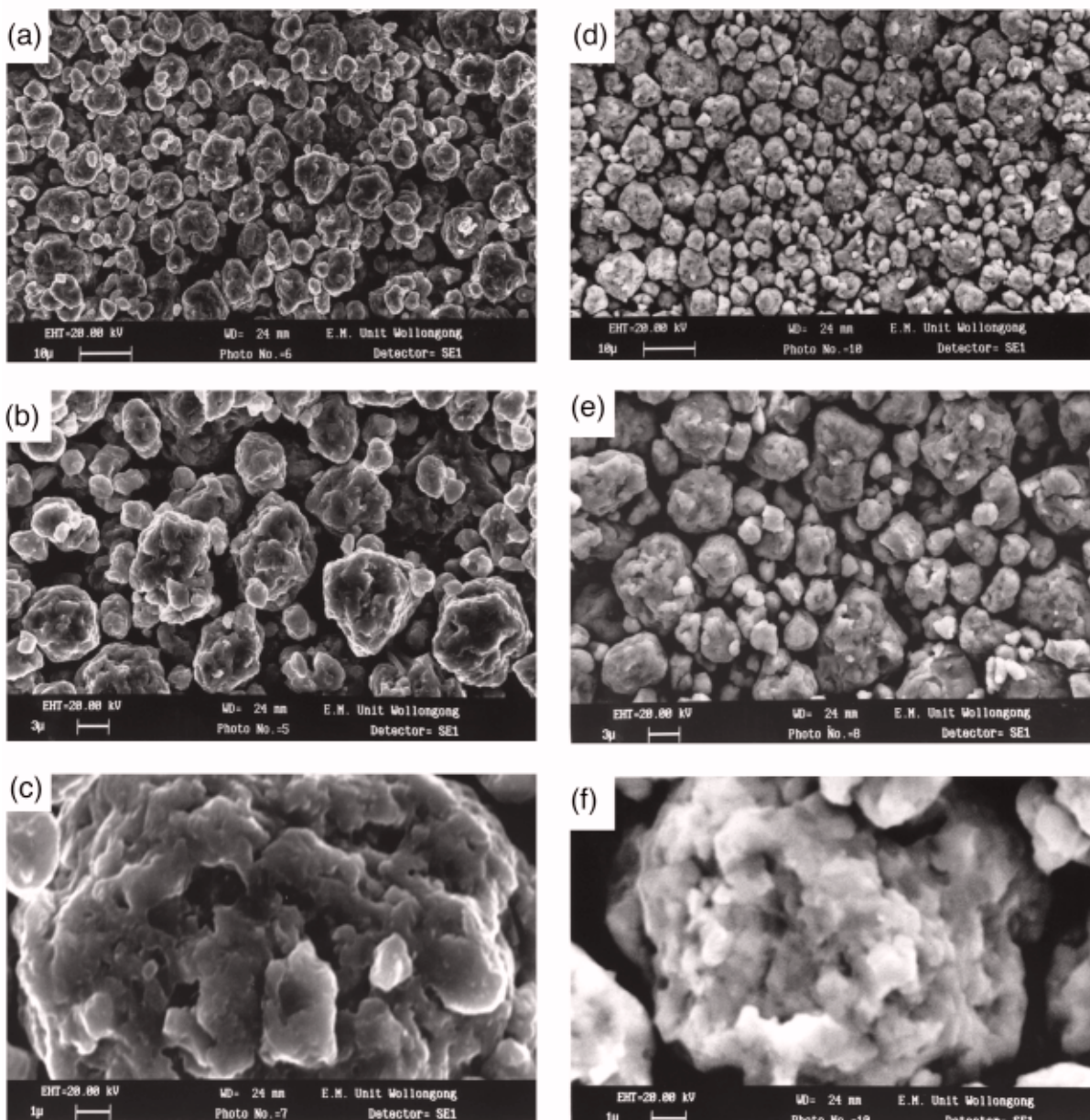


Figure 3. SEM images of MG- $Mg_{1.9}Al_{0.1}Ni_{0.8}Co_{0.1}Mn_{0.1}$ alloy after grinding for (a), (b), and (c) 50 and (d), (e), and (f) 120 h.

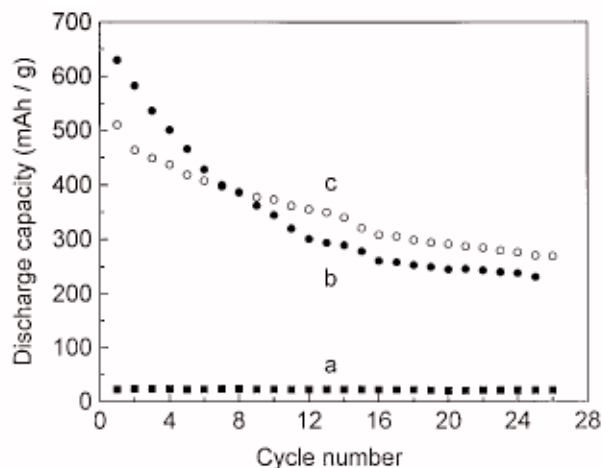


Figure 4. The discharge capacities and cycle life of $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ and MG- $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloys. (a) crystalline alloy; (b) alloy after grinding for 50 h; (c) alloy after grinding for 120 h.

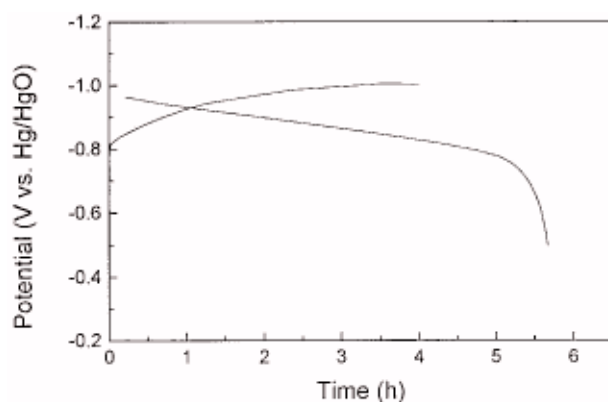


Figure 5. The charge-discharge curve at the 22nd cycle of the MG- $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloy after grinding for 120 h.

The decrease in the discharge capacities of the crystalline MNA alloy, MNA-50 and MNA-120 alloys after repeated charge-discharge cycles at room temperature is shown in Fig. 4. The discharge capacities of the MG-MNA alloys were calculated using the same basis as that used in the literature.^{6,7} The crystalline MNA alloy had a very low discharge capacity (about 22 mAh/g), but it was still higher than

that for crystalline Mg_2Ni reported in the literature^{6,7} even at a higher discharge current density (50 mA/g). This is attributed to the additions of the Co, Mn, and Al. On the other hand, the discharge capacities of the MG-MNA electrodes were much higher than that of their crystalline counterpart. For the first cycle, the discharge capacities of MNA-50 and MNA-120 alloys were 630 mAh/g and 510 mAh/g, respectively. The MNA-120 alloy had a lower initial discharge capacity and higher cycle life than MNA-50 alloy. These results are probably due to the differences in the surface structure and composition of the MG-MNA alloys. After grinding for 50 h, the layerlike structure and nonuniform Ni surface modification of the MNA-50 alloy allow a reaction to occur relatively easily during the electric charge process, so the electrode has higher initial discharge capacity but less cycle life. After grinding for 120 h, the MNA-120 alloy has a smooth amorphous Ni and MgNi surface structure which make it more resistant to alkaline corrosion. Thus, the MNA-120 electrode has a longer cycle life. These results suggest that mechanical grinding and element surface modification are effective methods for improving the charge-discharge capability and increasing the cycle life of Mg-based alloy negative electrodes.

Figure 5 shows the charge-discharge curve at the 22nd cycle of the MNA-120 alloy. It still has a plateau region at around -0.85 V vs. Hg-HgO electrode. The discharge capacity is still 280 mAh/g, somewhat higher than the MNA-50 alloy (243 mAh/g).

Conclusions

The discharge capacity of the electrode can be increased greatly by mechanical grinding with Ni powders. The mechanically ground $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloy has an amorphous structure which affects its charge-discharge capability. As the milling time increases, the initial discharge capacity of $\text{Mg}_{1.9}\text{Al}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ alloy decreases but its cycle life increases.

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