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Electrochemical characteristics of amorphous $Mg_{0.9}M_{0.1}Ni$ (M=Ni, Ti, Zr, Co and Si) ternary alloys prepared by mechanical alloying

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Abstract

$Mg_{0.9}M_{0.1}Ni$ (M=Ni, Ti, Zr, Co or Si) ternary alloys were prepared by mechanical alloying (MA). The XRD result showed that all ternary alloys were of amorphous structure, with a trace of substitution elements, except for Co. Electrochemical characteristics of all ternary alloys were studied which were compared to MA amorphous MgNi alloy. Experimental results showed that the ternary alloys had a large discharge capacity at room temperature but lower than that of the MA MgNi alloy. Partially substituting Mg with Ni, Ti, Co, Si could lead to the improvement of cyclic stability and high rate discharge capability. Over all, amorphous $Mg_{0.9}Ti_{0.1}Ni$ showed the best synthesis properties. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Mechanical alloying; Amorphous alloy; Mg–Ni alloy; Metal hydride; Electrochemical properties

1. Introduction

Magnesium-based alloys are promising hydrogen storage materials for their lighter weight, higher hydrogen weight percent (7.6%) of the metal hydrides and lower cost compare to other series of hydrogen storage materials. However, their poor electrochemically hydriding/dehydriding kinetics at room temperature prevents it from being practically used as the anode material for Ni–metal hydride rechargeable batteries [1]. Researchers have been making efforts to increase the rates of hydrogen absorption and desorption at lower temperature [2–5]. In the recent years, it was found that some amorphous Mg–Ni alloys prepared by mechanical alloying (MA) could absorb and desorb electrochemically a large amount of hydrogen at room temperature [6–8], which makes a new promise of research and application of Mg-based alloys. The range in which amorphous MA Mg_xNi_{100-x} alloys are formed extends from $x=30$ to 60 when pure elemental powders are alloyed by MA.

Nevertheless, the discharge capacities of amorphous Mg–Ni alloys degrade rapidly with the increase of cycle number. Moreover, their high rate dischargeabilities are poor [6]. The mechanism of degradation for amorphous Mg–Ni alloys and the methods to improve it have been widely studied at present [9–13], the studies showed that quick depression of capacity by cycle mainly attribute to the alloys' oxidative corrosion. As is well known, multicomponent alloying is one of the effective methods for modifying the properties of metal hydride; thus, the criteria to select substitutional element is its anti-oxidizing abilities but do less harm to capacities. In the present work, ternary $Mg_{0.9}M_{0.1}Ni$ alloys with Mg partially substituted by M (M=Ni, Ti, Zr, Co or Si) were prepared by MA, and their electrochemical characteristics were investigated.

2. Experimental

$Mg_{0.9}M_{0.1}Ni$ (M=Ni, Ti, Zr, Co and Si) ternary alloys were synthesized by mechanically alloying (MA). Elemental powders with sizes of 100~200 mesh and purity higher than 99% were used. In all experiments, the pure metal powder mixtures at designed compositions were milled in a conventional planetary ball mill with a ball to powder weight ratio of 15:1 under an Ar atmosphere for 120 h. The containers (50 ml in volume) and balls (5~10 mm in diameter) were made of stainless steel. The structure was characterized by X-ray diffraction.

Test electrodes were prepared by mixing the MA alloy

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powders with electrolytic copper powder (~200 mesh) in a weight ratio of 1:2 and cold pressed under a pressure of 18 MPa into pellets of 10 mm in diameter. Electrochemical measurements were carried out at 25°C by using a three-electrode-system cell consisting of the metal hydride working electrode, a NiOOH/$Ni(OH)_2$ counter electrode, and a Hg/HgO reference electrode. The electrolyte was 6 M KOH solution. In discharge capacity and cycle life tests, each negative electrode was charged at 50 mA/g for 12 h and discharged to -0.6 V (versus Hg/HgO, 6 M KOH) at 50 mA/g using an automatic galvanostatic charge–discharge unit. The circuit lay up for 10 min between each charging/discharging process.

3. Results and discussion

3.1. Structural characteristics

Fig. 1 shows the XRD patterns of the MA $Mg_{0.9}M_{0.1}Ni$ (M = Ni, Ti, Zr, Co or Si) ternary alloys. All alloys exhibit a broad diffuse peak at around 40~45 degree, which implies that the partial replacement of Mg in MgNi by the elements studied does not change the amorphous major phase structure. And all alloys exhibit a trace of elemental Ni and substitutional elements with the exception of Co. The sharp diffraction peaks attributed to the metal suggest that Ni and substitutional elements Ti, Zr and Si still remain partly in their crystalline state. However, Co has been completely amorphized.

3.2. Maximum capacity and charging/discharging characteristics

MA $Mg_{0.9}M_{0.1}Ni$ (M = Ni, Ti, Zr, Co or Si) ternary alloys possess good activation behavior, all alloys reach their maximum discharge capacity at the first cycle. Figs. 2 and 3 show the charge/discharge curves of ternary alloys in the first cycle. The electrochemical properties of ternary alloys are listed in Table 1. For comparison, Figs. 2 and 3 and Table 1 also list the relative properties of MA amorphous MgNi alloy.

From Figs. 2 and 3 and Table 1, we can see that all ternary amorphous alloys show higher capacity than AB_5 type hydrogen storage alloys at room temperature. This should be attributed to their amorphous structure. And the trace amount of metal Ni can further improve the electrocatalytic property. However, the maximum discharge capacity of all the ternary alloys is less than that of the MgNi alloy. Among the substitution elements, Ni, Co and Si cannot absorb hydrogen, but Ti and Zr are hydrogen absorbing elements as Mg, so it is reasonable that amorphous $Mg_{0.9}Zr_{0.1}Ni$ and $Mg_{0.9}Ti_{0.1}Ni$ show higher capacity than other ternary alloys. For example, the maximum discharge capacity of amorphous $Mg_{0.9}Zr_{0.1}Ni$ is 455.4 mAh/g, only 31 mAh/g less than that of amorphous MgNi alloy. If we define the potential relating to the half-maximum discharge capacity of alloys as their average charge/discharge potential, which was listed in Table1. We can see that all elements substituted lead to the average charge/discharge potential moving towards the negative

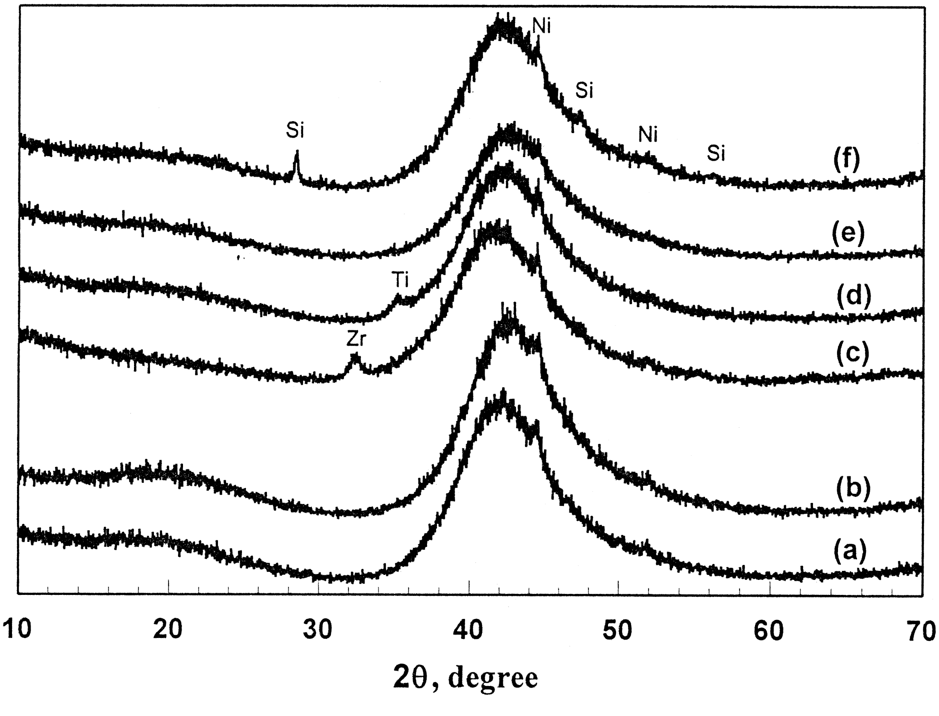

Fig. 1. The XRD patterns of amorphous $Mg_{0.9}M_{0.1}Ni$ (M = Ni, Ti, Zr, Co, Si) ternary alloys [(a) MgNi, (b) $Mg_{0.9}Ni_{1.1}$, (c) $Mg_{0.9}Zr_{0.1}Ni$, (d) $Mg_{0.9}Ti_{0.1}Ni$, (e) $Mg_{0.9}Co_{0.1}Ni$, (f) $Mg_{0.9}Si_{0.1}Ni$].

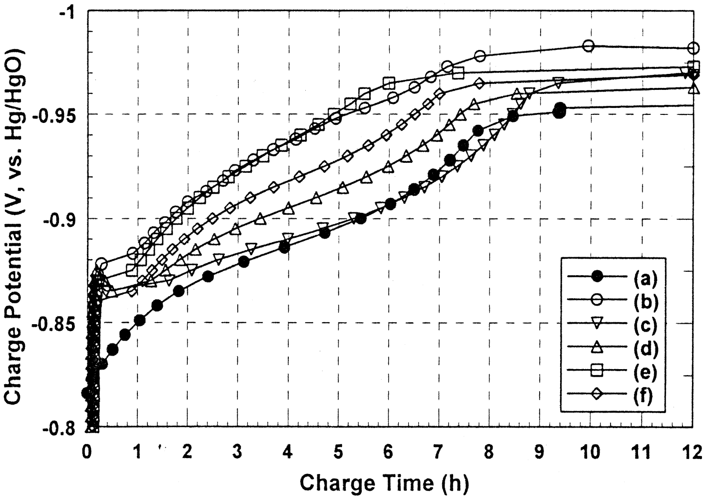

Fig. 2. The charge potential curves of amorphous alloys [(a) MgNi, (b) $Mg_{0.9}Ni_{1.1}$, (c) $Mg_{0.9}Zr_{0.1}Ni$, (d) $Mg_{0.9}Ti_{0.1}Ni$, (e) $Mg_{0.9}Co_{0.1}Ni$, (f) $Mg_{0.9}Si_{0.1}Ni$].

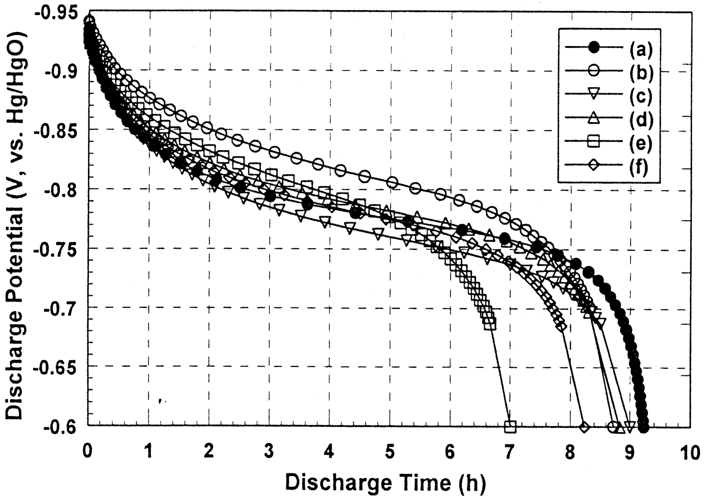

Fig. 3. The discharge potential curves of amorphous alloys [(a) MgNi, (b) $Mg_{0.9}Ni_{1.1}$, (c) $Mg_{0.9}Zr_{0.1}Ni$, (d) $Mg_{0.9}Ti_{0.1}Ni$, (e) $Mg_{0.9}Co_{0.1}Ni$, (f) $Mg_{0.9}Si_{0.1}Ni$].

potential direction except for Zr-substituting. Furthermore, all elements substituted increase the polarization of the amorphous MgNi alloy electrode, which can be obtained from the difference of the average charge/discharge potential, ΔV_{c-d}, which are also listed in Table 1. As to why amorphous $Mg_{0.9}Zr_{0.1}Ni$ alloys have the lowest average charge/discharge potential, maybe the stability of hydrogen in it is much higher. The poorest high rate dischargeability of $Mg_{0.9}Zr_{0.1}Ni$ mentioned later also confirms this point.

Table 1
The electrochemical properties of amorphous $Mg_{0.9}M_{0.1}Ni$ (M = Ni, Ti, Zr, Co or Si) ternary alloys

Alloys	C_{max} (mAh/g)	$N_{200\ mAh/g}$	$V_{av,c}$ (V versus Hg/HgO)	$V_{av,d}$ (V versus Hg/HgO)	ΔV_{c-d} mV
$Mg_{0.9}Ni_{1.1}$	401.1	27	−0.940	−0.815	125
$Mg_{0.9}Ti_{0.1}Ni$	438.9	34	−0.910	−0.785	125
$Mg_{0.9}Zr_{0.1}Ni$	455.4	16	−0.890	−0.770	120
$Mg_{0.9}Co_{0.1}Ni$	352.5	22	−0.930	−0.805	125
$Mg_{0.9}Si_{0.1}Ni$	413.2	31	−0.920	−0.790	130
MgNi	486.4	15	−0.820	−0.780	112

3.3. Cyclic stability

The changes of the discharge capacity of amorphous $Mg_{0.9}M_{0.1}Ni$ alloy with cycle number are depicted in Fig. 4. As seen from Fig. 4, the capacity of amorphous $Mg_{0.9}Zr_{0.1}Ni$ degrades rapidly, after 18 charge/discharge cycles its discharge capacity is lower than that of MgNi. For the alloys substituted by Ni, Ti, Co or Si, their discharge capacities are higher than that of amorphous MgNi after 9 charge/discharge cycles, thus showing better cyclic stability. When we use the cycle number that the alloy's capacity degrades to 200 mAh/g, $N_{200\ \mathrm{mAh/g}}$ which was also listed in Table 1, to value the cyclic stability of alloys, we can see all ternary alloys' stability are higher than that of amorphous MgNi. Above all, amorphous $Mg_{0.9}Ti_{0.1}Ni$ and $Mg_{0.9}Si_{0.1}Ni$ alloys can last more than 30 charging/discharging cycles before their capacities degrade to 200 mAh/g. Those results show the best cyclic stability of amorphous Mg-base hydrogen-storage-alloy electrode update.

The former studies showed that the capacity deterioration of amorphous Mg–Ni alloys could be mainly attributed to the oxidation of magnesium [6–10]. So we must try to prevent the element Mg from oxidation. Ti and Si can form thick, dense, passive oxides in alkaline solutions during the charge/discharge process, thus, improving the alloy's anti-oxidation ability. Ni is also resistant to oxidation. In the present text, ternary alloys show relatively good cyclic stability, which is also largely ascribed to high Ni content in the amorphous alloy. As for the amorphous MgNi alloy with partly substituted Ni by other elements, the improvement of cyclic stability is not remarkable when compared with our present work [12]. For the AB_5-type hydrogen storage alloy, cobalt restrains alloy corrosion caused by an alkaline electrolyte, thereby preventing the deterioration of the alloys. In the present work, Co-substitution can also prevent the deterioration of the amorphous Mg–Ni alloys. As for Zr-substitution, though it can improve the cycle life of the AB_5-type hydrogen storage alloy by precipitating at the grain boundaries to prevent cracking, this is not suitable for amorphous Mg–Ni alloys as exhibited in the present work.

3.4. High rate dischargeability

Fig. 5 shows that the discharge capacity of amorphous $Mg_{0.9}M_{0.1}Ni$ (M=Ni, Ti, Zr, Co, Si) ternary alloys at different discharge currents. All alloys' discharge capacities decreased linearly with an increase in the current. Table 2 lists the high rate discharge-abilities of amorphous $Mg_{0.9}M_{0.1}Ni$ ternary alloys. Except for $Mg_{0.9}Zr_{0.1}Ni$, all the other alloys show better high rate discharge-abilities than amorphous MgNi. If we use $C_{250\ \mathrm{mA/g}}/C_{50\ \mathrm{mAh/g}}$ to evaluate the high rate discharge-abilities of alloys, then the enhanced effect decreases with Co, Ni, Ti, Si, Zr in sequence. Above all, the $C_{250\ \mathrm{mA/g}}/C_{50\ \mathrm{mAh/g}}$ of amorphous $Mg_{0.9}Co_{0.1}Ni$ reaches 92.5%, comparable to AB_5-type hydride electrodes. The $C_{250\ \mathrm{mA/g}}/C_{50\ \mathrm{mAh/g}}$ of amorphous $Mg_{0.9}Ni_{1.1}$ reaches 80.43%. The exchange current densities of amorphous ternary alloys at discharge-state were exterminated by using the line-polarization method, which is also listed in Table 2. Seen from Table 2, we find that the exchange current density of $Mg_{0.9}Co_{0.1}Ni$ is the lowest though it shows the best high rate discharge capability. However, the exchange current density of $Mg_{0.9}Ti_{0.1}Ni$ (116.32 mA/g) is higher than that of the $Mg_{0.9}Ni_{1.1}$ alloy (95.01 mA/g), but its high rate capability (68.52%) is much lower than that of amorphous

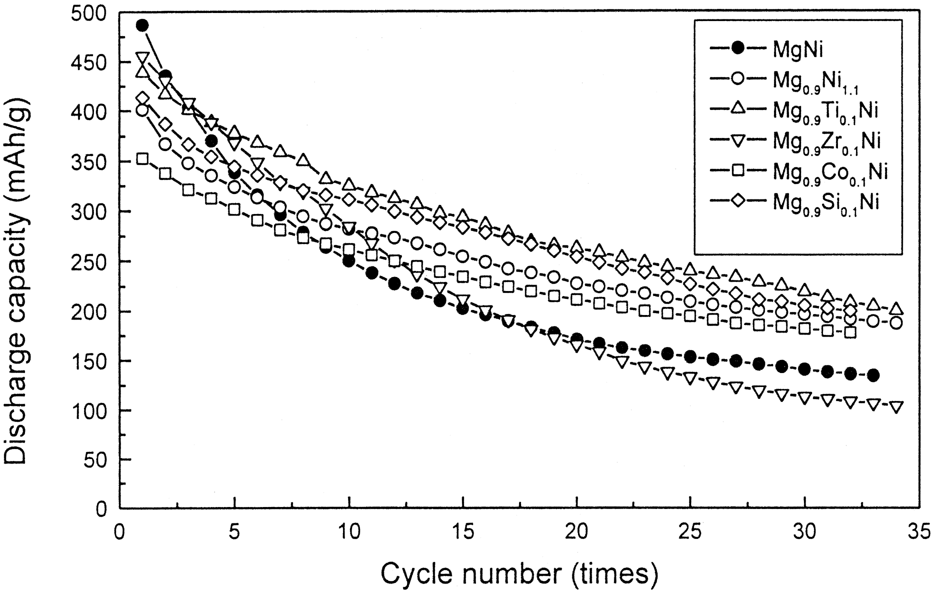

Fig. 4. Discharge capacity as a function of cycle number for amorphous MA $Mg_{0.9}M_{0.1}Ni$ (M=Ni, Ti, Zr, Co, Si) ternary alloys.

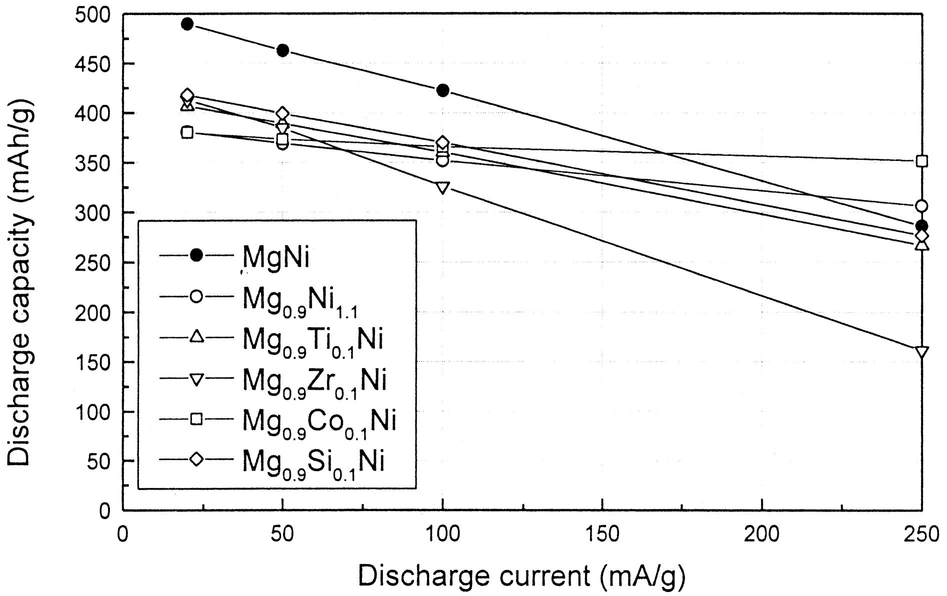

Fig. 5. The discharge capacities of amorphous $Mg_{0.9}M_{0.1}Ni$ (M=Ni, Ti, Zr, Co, Si) ternary alloys at different discharge currents.

Table 2
The high rate discharge abilities and the exchange current densities of amorphous $Mg_{0.9}M_{0.1}Ni$ (M=Ni, Ti, Zr, Co or Si) ternary alloys at 25°C

Alloys	$C_{250\ mA/g}/C_{100\ mA/g}$ (%)	$C_{250\ mA/g}/C_{50\ mA/g}$ (%)	I_0 (mA/g)
$Mg_{0.9}Ni_{1.1}$	87.06	80.43	95.01
$Mg_{0.9}Ti_{0.1}Ni$	74.03	68.52	116.32
$Mg_{0.9}Zr_{0.1}Ni$	49.52	41.95	67.53
$Mg_{0.9}Co_{0.1}Ni$	96.08	92.50	63.17
$Mg_{0.9}Si_{0.1}Ni$	74.72	66.11	87.82
MgNi	67.72	61.77	86.53

$Mg_{0.9}Ni_{1.1}$ (80.43%). In other word, the exchange current densities of the amorphous MA Mg–Ni alloy do not correspond with their high rate capabilities. It is connected with the kinetic mechanism of amorphous electrode alloys, which are under study now.

4. Conclusion

All $Mg_{0.9}M_{0.1}Ni$ (M=Ni, Ti, Zr, Co or Si) ternary alloys prepared by MA are amorphous structures, with a trace of substitution elements, except for Co. All amorphous ternary alloys reach their maximum capacity at the first charge/discharge cycle and show large discharge capacities at room temperature, but lower than that of the amorphous MgNi binary alloy. The amorphous ternary alloys show a more negative charge/discharge potential than that of amorphous MgNi with the exception of Zr-substitution alloy. The amorphous ternary alloys show better cyclic stability and high rate capability than that of the amorphous MgNi binary alloy with the exception of the Zr-substitution alloy. Over all, the amorphous $Mg_{0.9}Ti_{0.1}Ni$ can keep a 200 mAh/g capacity up to the 34th charge/discharge cycle; and shows the best synthesis properties.

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