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Synthesis of Nonstoichiometric Amorphous Mg-Based Alloy Electrodes by Mechanical Milling

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Nonstoichiometric amorphous Mg-Ni and Mg-Ni-V alloys were synthesized by mechanical milling the crystalline Mg$_2$Ni alloy with Ni and/or V powders. All the nonstoichiometric Mg-based alloys result in Mg-based alloy electrodes with very high discharge capacities by comparison with crystalline Mg$_2$Ni alloys. The results indicate that nonstoichiometric amorphous Mg-based alloys can be obtained either by increasing the Ni content, adding a range of other elements, or both, using a mechanical milling method. The nonstoichiometric Mg-based alloy electrodes studied have shown improved initial discharge capacities compared with the stoichiometric amorphous MgNi alloy. These results describe a method of achieving better Mg-based alloy electrodes with high discharge capacities and improved cycle life. The method enables a larger composition range to be achieved with a range of vanadium additions.

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**Experimental**

Alloy preparation and characterization.—The metal Ni (100 mesh, 99.7%) and V (-325 mesh, 99.5%) powders were obtained from the Aldrich Chemical Company. The induction melted (IM) Mg$_2$Ni alloy was supplied by Santoku Metal Industry Co., Japan. Mechanical milling was performed with a Fritsch (P5) planetary ball mill. The vials and balls were made from stainless steel and hardened steel, respectively. To obtain more active alloy powders, the Mg$_2$Ni alloy was mixed and ballmilled with Ni and V powders for a period of about 70 h at 200 rpm in an argon atmosphere. The alloy compositions are listed in Table I. After milling, the powders were examined by XRD. XRD analysis was conducted using a Philips PW1010 X-ray diffractometer with Cu Kα radiation. Morphologies and X-ray mapping analyses of the powdered alloys were conducted using a Leica Stereoscan 440 scanning electron microscope (SEM) and Oxford ISIS system using an OXFORD Link Pentafet detector.

**Fabrication of electrodes and electrochemical measurements.—**The IM Mg$_2$Ni alloy was crushed into powder and mixed with Ni powder in the weight ratio of 1:1 to make electrodes. The hydrogen storage alloy powders obtained from MM were also mixed with Ni powder in the weight ratio of 1:1 for electrode preparation. The hydride electrodes were fabricated by mixing the resultant powders with polyvinyl alcohol (PVA) solution and pasting them into a foamed nickel matrix, which acted as the current collector for the electrode. After being compressed, the hydride electrodes were immersed as negative electrodes in a 6 M KOH solution together with a NiOOH/Ni(OH)$_2$ counter electrode. A mercury oxide electrode (Hg/HgO) was used as the reference electrode. The electrochemical charge-discharge properties of the alloys were measured using a battery test unit controlled by a computer at 25°C. In the charge-discharge cycle tests, the charge cycle was commenced using a battery test unit controlled by a computer at 25°C.

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**Table I. The compositions of ballmilled alloys.**

<table>
<thead>
<tr>
<th>Mg$_2$Ni, Ni, and V ratio (molar)</th>
<th>Alloy formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Ni + Ni</td>
<td>MgNi(Mg$<em>{0.5}$Ni$</em>{0.5}$)</td>
<td>A</td>
</tr>
<tr>
<td>Mg$_2$Ni + 1.28 Ni</td>
<td>MgNi$<em>{1.14}$ (Mg$</em>{0.467}$Ni$_{0.533}$)</td>
<td>B</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.1 V</td>
<td>MgNiV$<em>{0.1}$ (Mg$</em>{0.476}$Ni$<em>{0.476}$V$</em>{0.048}$)</td>
<td>C</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.2 V</td>
<td>MgNiV$<em>{0.2}$ (Mg$</em>{0.455}$Ni$<em>{0.455}$V$</em>{0.09}$)</td>
<td>D</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.4 V</td>
<td>MgNiV$<em>{0.4}$ (Mg$</em>{0.417}$Ni$<em>{0.417}$V$</em>{0.166}$)</td>
<td>E</td>
</tr>
<tr>
<td>Mg$_2$Ni + 1.28 Ni + 0.1 V</td>
<td>MgNi$<em>{1.14}$V$</em>{0.1}$ (Mg$<em>{0.446}$Ni$</em>{0.446}$V$_{0.045}$)</td>
<td>F</td>
</tr>
</tbody>
</table>

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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 -0.6 V. The discharge capacities were calculated based on the total weight of the alloys.

**Results and Discussion**

**Mg-Ni alloys.**—The XRD pattern of the IM Mg$_2$Ni is shown in Fig. 1, which indicates a single Mg$_2$Ni phase. Figure 2 shows the XRD patterns of the IM Mg$_2$Ni alloy ballmilled with Ni powders in different ratios, indicating that homogenous amorphous MgNi and MgNi$_{1.14}$ were formed: Mg$_2$Ni + 1.28 Ni $\rightarrow$ 2MgNi$_{1.14}$. Orimo et al.\textsuperscript{13} reported that the high resolution TEM image and its diffraction pattern of compound Mg$_2$Ni ballmilled with Ni powder (molar ratio: 1:1, e.g., Mg-50 atom % Ni, or MgNi) shows that an amorphous structure was obtained. The ballmilled alloys of the composition of Mg-33 atom % Ni, Mg-38 atom % Ni, and Mg-43 atom % Ni only have a nanostructure or a mixture of partial nanostructure and partial amorphous structure.\textsuperscript{13} This means that decreasing the Mg content may cause more difficulty in obtaining an amorphous structure for Mg-Ni alloys. Our result indicates that an amorphous structure can be obtained even if the nickel content is increased.

The hydrogen storage alloy Mg$_2$Ni reacts with H$_2$ readily at 325°C and 300 Pa, and the reaction in the plateau region can be expressed by the equation: Mg$_2$Ni + H$_2$ $\rightarrow$ Mg$_2$NiH$_4$.\textsuperscript{14} The theoretical electrochemical capacity of hydride Mg$_2$NiH$_4$ is 999 mAh/g. However, the maximum hydrogen content of the amorphous MgNi region, 2.2 wt %, corresponds to a formula of MgNiH$_{1.9}$,\textsuperscript{13} and a calculated electrochemical capacity of 613 mAh/g.

The decrease in the discharge capacities of the crystalline IM Mg$_2$Ni alloy and the amorphous MgNi and MgNi$_{1.14}$ alloys after repeated charge-discharge cycles at a discharge current density of 50 mA/g is shown in Fig. 3. The discharge capacities of the alloys were calculated using their total weights. The crystalline IM Mg$_2$Ni alloy has a very low discharge capacity of only about 20 mAh/g (because of its poor hydriding kinetics at 25°C) while alloys A and B have much higher capacities. The initial discharge capacities of amorphous alloys A and B are approximately the same: 336 mAh/g, much higher than that of crystalline IM Mg$_2$Ni compound. After several charge-discharge cycles, the discharge capacities of both alloys A and B decrease rapidly. But nonstoichiometric amorphous alloy B has a slightly better cycle life than that of alloy A. This result encourages us to add other elements in a different way from traditional substitution, making nonstoichiometric Mg-based alloy electrodes.

**Nonstoichiometric Mg-Ni-V alloys.**—It has been well known since the 1960s that amorphous metals and alloys can be made by rapid quenching from the vapor or the liquid phase. A large number of investigations have shown that amorphous metals and alloys have the features of new alloy compositions and new atomic configurations which are totally different from those of crystalline alloys.

These features enable various kinds of characteristics to be achieved, such as excellent mechanical properties, useful physical properties, and unique chemical properties\textsuperscript{16-21} which have not been obtained for conventional crystalline alloys. Recently, solid-state amorphization by MA and MM have become the most effective methods for obtaining amorphous alloys.\textsuperscript{22-32} The amorphous composition range achievable by MA and MM is normally larger than that of other techniques. Lee and Koch\textsuperscript{33} have reported that the MA Ni-Nb alloy system has a wider amorphous composition range than that of melt quenching. Therefore, it seems likely that it would be possible to synthesize nonstoichiometric amorphous MgNi alloy by adding other elements to MgNi alloy using the MA or MM method.

The XRD patterns of nonstoichiometric alloys C, D, E, and F are shown in Fig. 4. The patterns indicate that alloys C, D, E, and F are amorphous alloys. This conclusion was also confirmed by the results of differential thermal analysis (DTA) and TEM electron diffraction. These solid reactions correspond to the following reaction

$$\text{Mg}_2\text{Ni} + x\text{Ni} + y\text{V} \rightarrow 2\text{MgNi}_{(x+1)/2}\text{V}_{y/2} \quad [1]$$

where \(x\) and \(y\) are molar fractions of Ni and V, respectively. Thus,
different amounts of vanadium can be added to the amorphous Mg-Ni alloy to make a range of nonstoichiometric Mg-based alloys without changing their basic amorphous structure.

Figure 5a shows the SEM micrograph of the alloy C powders while Fig. 5b is the micrograph of a larger particle of alloy C. Figure 5c and d are X-ray maps in the same field of V and Ni, respectively. The particle sizes of alloy C powders are around 5-12 μm. The powder surface of alloy C (Fig. 5b) looks concavo-convex which should be a more activated amorphous surface with a high catalytic activity. The V and Ni concentrations in alloy C are fairly evenly distributed, showing that the alloy C has a homogenous amorphous MgNiV_{0.1} component and indicating that the MM nonstoichiometric Mg-based alloy can achieve a uniform amorphous structure.

The discharge capacities of the alloys A, C, D, E, and F after repeated charge-discharge cycles at a discharge current density of 50 mA/g are shown in Fig. 6. The discharge capacities were calculated based on the total weight of the alloys. Compared with the discharge capacity of the amorphous stoichiometric alloy A (336 mAh/g), the nonstoichiometric alloys C, D, E, and F have higher discharge capacities and better cycle characteristics. The initial discharge capacities of alloys C, D, E, and F are 414, 357, 361, and 362 mAh/g, respectively. The nonstoichiometric alloys D, E, and F have almost the same discharge capacity and cycle life, while alloy C has the highest discharge capacity and best cycle life. This shows that nonstoichiometric additions of vanadium can increase both the discharge capacity and cycle life of amorphous MgNi alloy electrodes, and that the amorphous MgNi alloy containing 0.1 molar addition of vanadium has the best electrode properties. These initial discharge capacities are higher than those of AB_{5}-type and AB_{2}-type hydride electrodes. Increasing the V content did not alter the electrode properties of the amorphous MgNi alloys. If the discharge capacities of the alloys are calculated based on MgNi content,^{5-8} the capacity of alloy C will be 658 mAh/g at a discharge current density of 79 mA/g. The nonstoichiometric addition of vanadium and nickel in MgNi

Figure 4. XRD patterns of nonstoichiometric alloys C, D, E, and F.

Figure 5. SEM micrograph of (a) the MgNiV_{0.1} alloy powders. (b) The micrograph of a larger particle of MgNiV_{0.1} alloy, X-ray mapping of (c) V and (d) Ni of MgNiV_{0.1} alloy in the same field, respectively.
improved initial discharge capacities compared with the stoichiometric amorphous MgNi alloy. These results describe a method of achieving better Mg-based alloy electrodes with high discharge capacities. The method enables a larger composition range to be achieved with a range of vanadium additions.

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**References**