



Effect of nanostructure and partial substitution on gas absorption and electrochemical properties in Mg₂Ni-based alloys



Huaiyu Shao ^{a,*}, Xingguo Li ^{b,**}

^a International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan

^b Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT

Mg₂Ni-based alloys have been intensively investigated as gaseous hydrogen absorption materials and negative electrode materials for Nickel-Metal Hydride (Ni–MH) battery. In this work, three Mg₂Ni-based samples (micrometer Mg₂Ni, nanometer Mg₂Ni and nanometer Mg₂Ni_{0.75}Cu_{0.25}) were synthesized from Mg, Ni and Cu nanoparticles and commercially available micrometer Ni particles. The metal nanoparticles were fabricated by hydrogen plasma metal reaction technique. The structure and morphology of these three Mg₂Ni-based samples were studied. Gaseous hydrogen absorption and electrochemical properties of these samples were investigated and compared. Amongst these three samples, the nanometer Mg₂Ni shows best gas absorption kinetics of 3.0 wt.% in 1 min under 4 MPa hydrogen at 623 K; the nanometer Mg₂Ni_{0.75}Cu_{0.25} sample shows a highest first cycle electrochemical capacity of 346 mAh/g. The effect of nanostructure and partial substitution on gas absorption and electrochemical performance was clarified.

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1. Introduction

Burning fossil fuels produces carbon dioxide, which greatly causes the greenhouse effect. People are trying to find a clean energy solution. Hydrogen is thought to be the most promising green energy carrier [1,2]. Nevertheless, one must find a convenient and safe way to store hydrogen before the real hydrogen energy society may be realized. Mg-based alloys are considered to be promising candidates for hydrogen storage because of the advantages such as great abundance, low cost and high hydrogen capacity [3–5], especially when the currently commercialized AB₅ and AB₃-type alloys are with a much lower hydrogen capacity and relatively higher price due to the rare earth element used in these alloys. As gaseous hydrogen storage materials, Mg-based materials are suffering the obstacles of poor kinetics and too stable hydrogen bonding although some recent progresses have been made to tackle these issues [6–13]. One of the potential applications of Mg-based alloys is as negative electrode materials in Nickel-Metal Hydride (Ni–MH) battery [14]. However, the electrochemical cycle

characteristics of Mg-based alloys fail to meet the requirements for practical application because Mg-based alloys are easy to be oxidized in alkaline solution electrolyte used in the battery [15,16]. This is one reason why the reported experimental discharging capacities are always much lower than the exciting theoretical value of 999 mAh/g for the Mg₂Ni compound.

To improve electrochemical properties of Mg–Ni-based alloys, a large number of methods have been employed. Many efforts have been made to apply melt spinning [17,18], magnetron sputtering [19,20], laser sintering [21–23] and mechanical alloy (MA) [24,25] for material synthesis [26–31]. Some work has been tried on partial substitution of Mg or Ni by other elements or addition of some catalytic materials [15,32–39]. Some researchers have tried modifying the relative molar ratio of Mg to Ni in the alloys [24,40] and some have tried surface modification of the alloys by techniques such as nickel coating [27,41], fluorination treatment and acid treatment [42,43] to elevate the performances. But up to now, few satisfying results have emerged to make the materials ready for real applications.

The authors have reported synthesis of Mg₂Ni nanoparticles from Mg and Ni nanoparticles produced by hydrogen plasma-metal reaction method [44–46]. Some work has been done on gaseous hydrogen storage property study of these nanostructured Mg-based materials [15]. Here we compare the work on gaseous

* Corresponding author.

** Corresponding author.

E-mail addresses: h.shao@i2cner.kyushu-u.ac.jp, shaohuaiyu@gmail.com (H. Shao), xgli@pku.edu.cn (X. Li).

hydrogen absorption and electrochemical properties study in three samples-micrometer Mg_2Ni (named micro- Mg_2Ni , hereafter), Mg_2Ni nanoparticle sample (nano- Mg_2Ni) and $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$ nanoparticle sample (nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$) to clarify the effect of downsizing from micrometer scale to nanometer one and partial substitution of Ni by Cu on gaseous absorption and electrochemical properties of these materials.

2. Experimental section

2.1. Preparation of the Mg_2Ni -based alloys

Three alloys (micro- Mg_2Ni , nano- Mg_2Ni , nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$) were prepared from Mg, Ni and Cu particles under the conditions shown in Table 1. The nano- Mg_2Ni alloy and the nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$ alloy were synthesized from Mg, Ni and Cu metal nanoparticles. These nanoparticles were prepared from bulk metals by hydrogen plasma-metal reaction method [47]. Detailed introduction of the equipment and preparation process of these metal nanoparticles can be found here [45]. By this technique, Mg, Ni and Cu nanoparticles were obtained with average sizes of 300, 30 and 50 nm, respectively. A mixture of Mg and Ni (or Mg, Ni and Cu for nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$) nanoparticles in 2:1 (or 2:0.75:0.25) molar ratio was immersed in acetone and then mixed by an ultrasonic homogenizer for 30 min. After being dried by a blower, the metal mixture was pressed into pellets under a pressure of about 75 MPa by a press for 30 s. The pellets were cracked into pieces, as starting samples for preparation of nano- Mg_2Ni (or nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$) compound. After the sample was put into a reactor, the system was evacuated to 10^{-3} Pa. Then the sample was heated up to 623 K and a hydrogen pressure of 4.0 MPa was provided to make the mixture sample react with hydrogen for 2 h (5 h for nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$). After that, the system was evacuated again, kept for 1 h and then cooled to room temperature.

The micro- Mg_2Ni alloy sample was prepared from the Mg nanoparticles synthesized by hydrogen plasma metal reaction and 200 mesh Ni particles (ca. 75 μm). The mixture of 300 nm Mg nanoparticles and 75 μm Ni in a molar ratio of 2:1 was immersed in acetone and mixed by an ultrasonic homogenizer for 30 min. After being dried, the mixture was pressed under a pressure of 75 MPa. The obtained pellets were cracked into pieces, as starting materials for preparation of the micro- Mg_2Ni . After the mixture sample was put into a tube furnace, the system was evacuated to 0.1 Pa. A flowing argon atmosphere of 0.1 MPa was provided and then the sample was heated to 773 K, kept for 3 h and then cooled to room temperature.

2.2. Characterization of the alloys

The structural analysis of the samples before and after synthesis reactions was carried out by X-ray diffraction (XRD) using an automatic Rigaku X-ray diffractometer with monochromatic Cu $K\alpha$ radiation. The measurements were conducted at a scanning rate of $4^\circ/\text{min}$ using a generator voltage of 40 kV and a current of 100 mA. The size distribution and morphology of samples were observed by scanning electron microscopy (SEM) on an Amray FE-1910 and

transmission electron microscopy (TEM) on a JEM-200CX operating at 160 kV.

2.3. Hydrogen gas absorption and electrochemical measurements

A conventional pressure-volume-temperature technique, which means measuring hydrogen content versus time by recording the change of hydrogen gas pressure in a constant volume, was used to obtain the hydrogen absorption curves of the alloys. The electrochemical measurements of these Mg_2Ni -based alloys were conducted in a prototype Ni-MH battery. The test electrodes were fabricated following these procedures. About 250 mg alloy powders (micro- Mg_2Ni , nano- Mg_2Ni and nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$) and 1 g electrolytic nickel powders (nanoparticle powders with an average size of 30 nm or micrometer powders of 75 μm , as conductive agent) were mixed and pressed into 2×2 cm anode under a pressure of 3 MPa for 1 min. The positive electrode was prepared using $\text{Ni}(\text{OH})_2$ as the active material, 10% poly (vinyl alcohol) and 15% polytetrafluoroethylene (PTFE) as binder, and 2×2 cm nickel foam sheet as current collector. The negative electrode was sandwiched with these two positive ones in a small cell to form a test battery. The electrolyte used was 6 M KOH + 1 M LiOH aqueous solution. In order to examine the electrochemical properties of the negative electrodes, the test batteries were designed for a negative capacity-limited system. The batteries were charged at 50 or 100 mA/g for 24 or 12 h and discharged at 50 or 100 mA/g to a cutoff voltage of 0.8 V on a PCBT-138 equipment (Wuhan Lisun, China). All the measurements were conducted at room temperature. Table 2 shows the measurement information of six prototype battery tests.

3. Results and discussion

3.1. XRD patterns

From Fig. 1(a), we can see that 300 nm Mg nanoparticles and 75 μm Ni powders react under 0.1 MPa argon at 773 K to form the micro- Mg_2Ni alloy. The alloy has a hexagonal structure (JCPDS: 35-1225) and the lattice constants of this Mg_2Ni compound are $a = 5.212 \text{ \AA}$ and $c = 13.257 \text{ \AA}$. The reflection peaks are sharp, which indicates micrometer size of the sample. The preparation in such simple conditions (at 773 K and under 0.1 MPa argon for 3 h) should ascribe to the Mg nanoparticles used as starting materials. It makes the mixture more homogeneous and makes the particles more easily to transfer and diffuse during solid state reaction. Fig. 1(b) is the obtained nano- Mg_2Ni alloy. The peak broadening indicates a size around 50 nm [45,46]. The nano- Mg_2Ni has the same structure (JCPDS: 35-1225) with the micro- Mg_2Ni . The lattice constants of the nano- Mg_2Ni are $a = 5.209 \text{ \AA}$ and $c = 13.240 \text{ \AA}$, which are a little smaller than the ones of the micro- Mg_2Ni . The difference is thought to be due to the different sizes of the metal particles used for synthesis and the different preparation processes. From Fig. 1(c), we can see that the obtained nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$ crystallizes with a Mg_2Ni -type structure and the lattice constants ($a = 5.217 \text{ \AA}$, $c = 13.397 \text{ \AA}$) are a little larger than those of the obtained nano- Mg_2Ni . This is due to the partial substitution of Ni by Cu. It seems the factor that Ni has a larger atomic radius than Cu is not in

Table 1
Synthesis conditions for the micrometer Mg_2Ni , nanometer Mg_2Ni and nanometer $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$ alloy samples.

Sample	Starting material	Atmosphere	Temperature (K)	Time (h)
Micro- Mg_2Ni	300 nm Mg, 75 μm Ni	0.1 MPa argon	773	3
Nano- Mg_2Ni	300 nm Mg, 30 nm Ni	4 MPa hydrogen	623	2
Nano- $\text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25}$	300 nm Mg, 30 nm Ni, 50 nm Cu	4 MPa hydrogen	623	5

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