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Effects of surface and bulk modifications on electrochemical and physicochemical characteristics of MgNi alloys

C. Iwakura[a,*], H. Inoue[a], S. Nohara[a], R. Shin-ya[b], S. Kurosaka[a], K. Miyanohara[a]

[a]Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
[b]Sumitomo Metal Technology, Fusocho 1-8, Amagasaki, Hyogo 660-0891, Japan

Abstract

Effects of partial substitution of Mg in MgNi with both Ti and V and subsequent surface modification by ball-milling with graphite on electrochemical and physicochemical characteristics of amorphous MgNi alloys were investigated. It was found from thermogravimetry (TG) that hydrogen desorbability of the MgNi alloys was improved by either partial substitution with both Ti and V or surface modification with graphite, and that the combination of the partial substitution and the subsequent surface modification enhanced the hydrogen desorbability further. In charge–discharge cycle tests, the partial substitution with Ti and V or surface modification with graphite suppressed the decay of discharge capacity with increasing cycle number. $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy modified with graphite exhibited further improved cycle performance as compared with either unmodified $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy or MgNi alloy modified with graphite. These results indicate that modification of both bulk and surface of the MgNi alloys is very effective in improving hydrogen desorbability and charge–discharge cycle performance of the alloys.

Keywords: MgNi alloy; Amorphous; Nickel–metal hydride battery; Surface modification; Graphite

1. Introduction

Mg-based hydrogen storage alloys are very attractive materials for energy conversion and storage. Nevertheless, high temperature is generally required for the reversible absorption and desorption of hydrogen in Mg-based alloys. Recently, many efforts have been made to improve their hydriding–dehydriding and charge–discharge characteristics from a practical point of view. Lei et al. [1,2] and our group [3,4] reported that amorphous MgNi alloys prepared by mechanical alloying (MA) could charge and discharge even at room temperature, which presented a new possibility for the application of Mg-based alloys in nickel–metal hydride batteries. For Mg_2Ni alloys, Zaluski et al. [5], Cui et al. [6,7], Orimo et al. [8,9], Kohno et al. [10] and our group [11,12] reported that their hydriding–dehydriding and charge–discharge characteristics were markedly improved by the formation of a nanocrystalline or amorphous structure and/or the modification with another material by using a ball mill.

However, decay of the discharge capacity of amorphous Mg-based alloys prepared by these methods with increasing cycle number is a serious problem. It may be mainly due to the oxidation of the alloy surface during the charge–discharge cycling in alkaline solution [2,13]. It was reported in our previous paper that surface modification of the MgNi alloys by ball-milling with graphite improve their electrochemical characteristics including charge–discharge cycle performance [3]. Moreover, our group also reported that MgNi alloy with Mg partially substituted with both Ti and V showed better cycle performance than one partially substituted with either Ti or V [14]. Therefore, in order to improve the cycle performance further, the combination of the partial substitution with foreign elements and surface modification with other materials is expected to be very effective. In this work, amorphous MgNi alloys were partially substituted with both Ti and V and subsequently modified by ball-milling with graphite, and then electrochemical and physicochemical characteristics of the composites were investigated.

2. Experimental

MgNi and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloys were prepared from Mg, Ni, Ti and V mixed powders (total mass of 1 g) by MA under Ar atmosphere using a planetary mill with an

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*Corresponding author. Tel./fax: +81-722-549-283.
E-mail address: iwakura@chem.osakafu-u.ac.jp (C. Iwakura).

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acceleration of ca. 30 m s^{-2} for 36 h. Surface modification of resulting alloy powders was carried out by ball-milling with graphite (mass ratio to alloy: 0.1) with an acceleration of ca. 30 m s^{-2} for 10 min. Structure of the alloys and composites was characterized by X-ray diffractometry. For the investigation of dehydriding characteristics, TG on the samples after being sufficiently hydrided was carried out under Ar flow with the heating rate of 10°C min^{-1}. Detailed procedures of these measurements were the same as described in our previous paper [15].

Each sample powder was mixed with Cu powder in mass ratio of 1:3 and 0.4 g of the mixture was pressed under a pressure of 8×10^3 kgf cm^{-2} at room temperature for 1 min. After that the resulting pellet was covered with a sheet of Ni mesh and soldered to a Ni wire to prepare a negative electrode. Charge–discharge cycle tests of the alloy electrodes were carried out in (6 M KOH+1 M LiOH) solution at 30°C. Each negative electrode was charged at 100 mA g^{-1} for 6 h and discharged to −0.6 V vs. Hg/HgO at 50 mA g^{-1}. After every charging, the circuit was opened for 10 min. Details of electrochemical measurements were the same as described in our previous paper [16].

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns for MgNi, $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$, MgNi–graphite composite and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite. For the MgNi alloy, the sole broad peak was observed in its diffraction pattern, suggesting that the alloy prepared by MA has an amorphous structure. This was also proved from TEM image and electron diffraction pattern in our previous paper [4]. In the case of the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy, the diffraction pattern was similar to that for the MgNi alloy, and no visible peaks identified as Ti, V or compounds which consist of Ti and/or V were observed. This suggests that the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy prepared by MA also has an amorphous structure. Moreover, diffraction patterns for the MgNi–graphite and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composites showed only peaks attributed to the amorphous MgNi or $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy and graphite. This indicates that in this ball-milling condition no new compounds are formed by ball-milling the MgNi or $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy with graphite.

TG curves of MgNi, $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$, MgNi–graphite composite and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite after being hydrided are shown in Fig. 2. A weight loss and a slight weight gain in high temperature region of each TG curve are due to hydrogen desorption of the hydrided sample and oxidation of the alloy surface by residual oxygen, respectively. In the case of the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy and the MgNi–graphite composite, hydrogen was desorbed at lower temperature as compared with the case of the MgNi alloy. This indicates hydrogen desorbability is promoted by either introduction of Ti and/or V or surface modification with graphite. Moreover, dehydriding temperature for the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite was lower than that for either the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy or the MgNi–graphite composite. From this result, it is found that the partial substitution with Ti and V and the subsequent surface modification with graphite are more effective in improving hydrogen desorbability of the MgNi alloy.

Discharge curves (1st cycle) at 30°C of MgNi, $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$, MgNi–graphite composite and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite electrodes are shown in Fig. 3. In all cases, a plateau of the potential caused by the oxidation of absorbed hydrogen was observed, and the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy and the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite showed more nega-

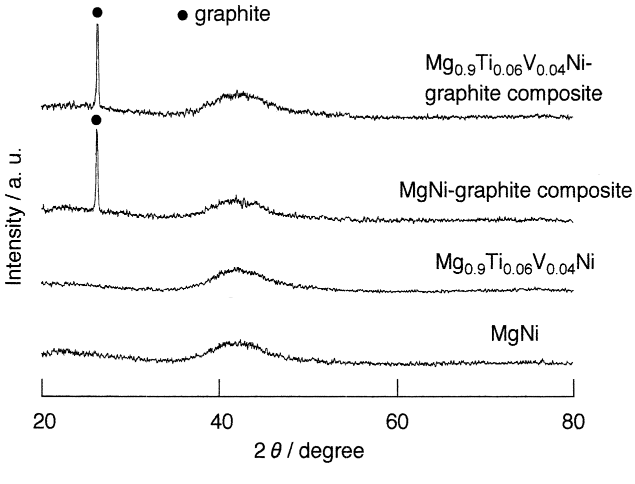

Fig. 1. X-ray diffraction patterns of MgNi, $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$, MgNi–graphite composite and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite.

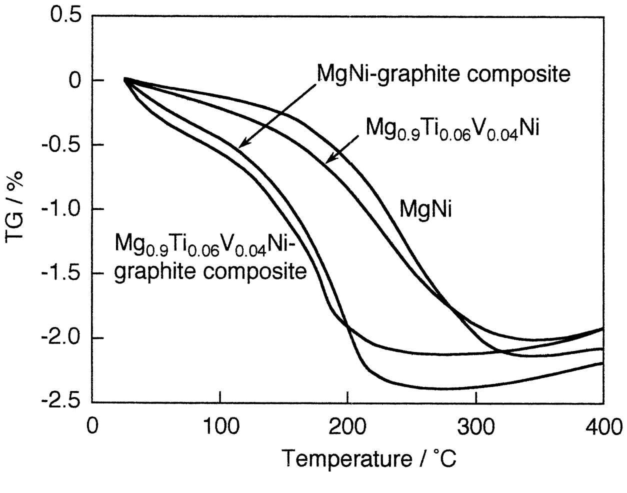

Fig. 2. TG curves for dehydriding of hydrided MgNi, $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$, MgNi–graphite composite and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite. Heating rate: 10°C min^{-1}.

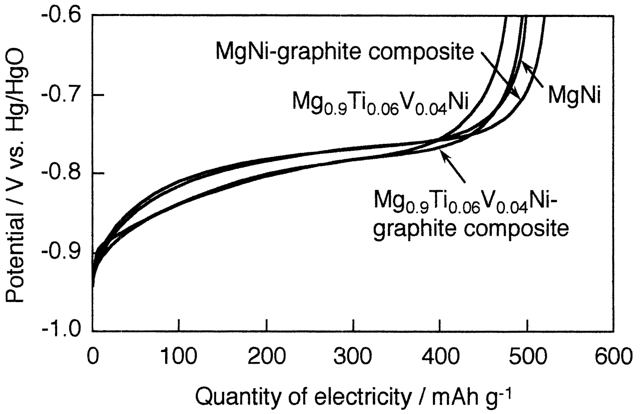

Fig. 3. Discharge curves (1st cycle) at 30°C of MgNi, $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$, MgNi–graphite composite and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite electrodes.

tive plateau potential than the MgNi alloy and the MgNi–graphite composite, respectively. This indicates that hydrogen desorbability of the MgNi alloy is improved by partial substitution of Mg with Ti and/or V, probably due to the increase in equilibrium pressure of hydrogen. In the case of surface modification of the MgNi and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloys with graphite, the discharge capacity was slightly increased as compared with the alloys before surface modification, and the MgNi–graphite composite exhibited the discharge capacity of ca. 520 mAh g^{-1} in this experimental condition. On the other hand, the plateau of the potential was hardly changed by the surface modification. In our previous paper, the result similar to this was observed for the MgNi alloy and MgNi–graphite composite electrodes in a different condition [3]. Furthermore, it was reported that the rate of hydrogen absorption was greatly increased by the surface modification with graphite [17], which was ascribed to an increase in the Ni/Mg ratio on the alloy surface [18]. Judging from these data, it can be inferred that the improvement in hydrogen desorbability by the surface modification with graphite, which was indicated from the results of TG, may be due to enhanced kinetics of hydrogen desorption.

Fig. 4 shows discharge capacities at 30°C as a function of cycle number. In the case of the MgNi alloy, discharge capacity decreased seriously with the increase in cycle number. The decay of discharge capacity was suppressed by either partial substitution with both Ti and V or surface modification with graphite as can be seen from this figure. Especially, the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy showed much slower capacity decay than the MgNi alloy. It may be ascribed to suppression of the formation of $Mg(OH)_2$ on the alloy surface by the preferential oxidation of Ti and V as reported previously [13,14]. Moreover, the combination of the partial substitution and the subsequent surface modification improved the cycle performance of the MgNi alloy further. As considered from the data described above, this may be due to the further improvement in the reversibility for hydrogen absorption and desorption and the corrosion resistance by surface modification of the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy with graphite. In order to clarify the reason for the improved characteristics, further detailed investigation is now in progress.

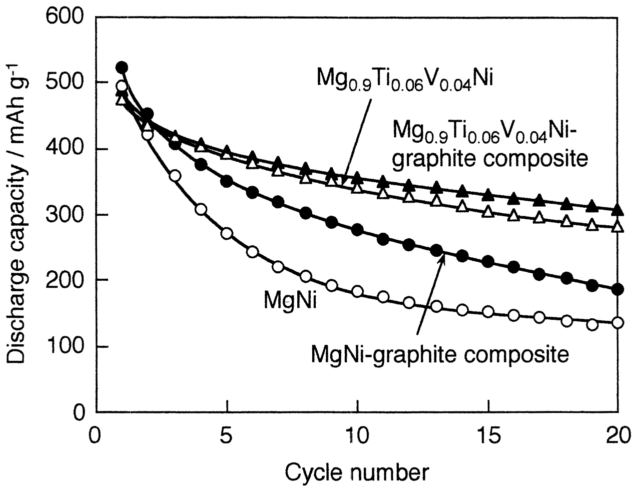

Fig. 4. Discharge capacities at 30°C as a function of cycle number for MgNi, $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$, MgNi–graphite composite and $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite electrodes.

In summary, it was found that the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$–graphite composite exhibited enhanced hydrogen desorbability and charge–discharge cycle performance in comparison with the MgNi alloy, the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy and the MgNi–graphite composite. From these results, it was indicated that surface and bulk modifications by the combination of the partial substitution with both Ti and V and the subsequent surface modification with graphite were very effective in improving electrochemical and physicochemical characteristics of the amorphous MgNi alloys.

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