INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–6

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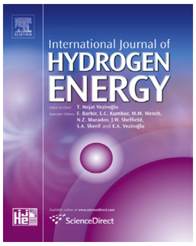

Effect of Ti substitution on electrochemical properties of ZrNi alloy electrode for use in nickel-metal hydride batteries

Akihiro Matsuyama [a,b,*], *Hironori Mizutani* [a], *Takumi Kozuka* [a], *Hiroshi Inoue* [b]

[a] *Advanced and High Functional Products Development Division, Aichi Steel Corporation, Tokai, Aichi 476-8666, Japan*

[b] *Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan*

ARTICLE INFO

Article history:
Received 11 January 2017
Received in revised form
14 March 2017
Accepted 19 March 2017
Available online xxx

Keywords:
ZrNi
Hydrogen storage alloy
Negative electrode
Nickel-metal hydride battery
Ti substitution

ABSTRACT

Crystal structure and electrochemical properties of the $Zr_{1-x}Ti_xNi$ ($0.05 \le x \le 0.5$) alloys were investigated. X-ray diffraction spectra showed that the primary phase of all $Zr_{1-x}Ti_xNi$ alloys had the *B*33-type orthorhombic crystal structure, which was characteristic of ZrNi, and the unit cell volume of the primary phase linearly decreased with an increase in the x value. In the charge–discharge tests with the $Zr_{1-x}Ti_xNi$ alloy negative electrodes, the initial discharge curves for the alloys with $x \ge 0.3$ had two plateaus. Both plateau potentials negatively shifted with an increase in the *x* value. The initial discharge capacity for the $Zr_{0.6}Ti_{0.4}Ni$ alloy negative electrode was 349 mAh g^{-1} at 25 mA g^{-1} and 333 K, which was the highest in this study. The high-rate dischargeability and cycle performance were also improved by the partial replacement of Zr by Ti.

Introduction

Rare earth-based hydrogen storage alloys such as AB_5-type ($LaNi_5$) alloys [1,2] and AB_3-type (La_2MgNi_9) superlattice alloys [3,4] are practically used as the negative electrode active materials for nickel-metal hydride (Ni-MH) batteries. The Ni-MH batteries have been commercialized as power sources for hybrid electric vehicles (HEVs), fuel cell vehicles (FCVs) and alternatives to dry cells because they were excellent in safety, cycle life, storage characteristic, rate capability, etc. [5]. To improve the fuel consumption of HEVs and FCVs, the energy density of Ni-MH batteries needs to be greatly improved. For this purpose, as the positive electrode active material, layered double hydroxide (LDH) with α-phase structure was developed [6,7]. As for the negative electrode active material, new hydrogen storage alloys whose discharge capacity was higher than the AB_5- and AB_3-alloy negative electrodes (320 and 360 mAh g^{-1}) have been developed. For instance, AB_2-type (ZrM_2 M = Mn, Cr, V) Zr-based Laves phase alloys whose

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* *Corresponding author*. Advanced and High Functional Products Development Division, Aichi Steel Corporation, Tokai, Aichi 476-8666, Japan. Fax: +81 52 603 9741.

E-mail address: a-matsuyama@he.aichi-steel.co.jp (A. Matsuyama).

http://dx.doi.org/10.1016/j.ijhydene.2017.03.119
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Please cite this article in press as: Matsuyama A, et al., Effect of Ti substitution on electrochemical properties of ZrNi alloy electrode for use in nickel-metal hydride batteries, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.03.119

discharge capacity was about 400 mAh g^{-1} were actively investigated [8,9]. On the contrary, another Zr-based alloy, AB-type ZrNi alloy, could store 2.0 mass% H_2 [10], which corresponds to theoretical electrochemical capacity of 536 mAh g^{-1}, so it is expected to be a promising candidate as the negative electrode active material. Recently, we have reported that the initial discharge capacity of the ZrNi alloy negative electrode was 21 mAh g^{-1} at 333 K, but it was increased to 320 mAh g^{-1} by the boiling alkaline treatment [11]. However, the experimental discharge capacity was much lower than the theoretical one, because the monohydride (β-ZrNiH), an intermediate product in the dehydrogenation process of the trihydride (γ-$ZrNiH_3$), was too stable to release hydrogen [12]. Therefore, the monohydride needs to be destabilized for improving hydrogen desorbability or discharge capacity. So far, nanocrystallization [13,14] and amorphization [14,15] were effective for the destabilization of hydrides. Meanwhile, when the unit cell volume of a hydrogen storage alloy is decreased or the lattice of the alloy is shrunk, its hydrides are destabilized [8,16]. Commonly, the lattice shrinkage can be realized by the partial substitution of alloy constituents with foreign metals whose atomic radii are smaller [8,16,17]. In this study, the Zr constituent in the ZrNi alloy was partially replaced with Ti whose atomic radius is smaller than Zr, and the effect of Ti substitution on electrochemical properties of ZrNi was clarified, which has never been performed so far.

Experimental

Preparation and crystal structure measurement of the $Zr_{1-x}Ti_xNi$ ($0.05 \le x \le 0.5$) alloys

The $Zr_{1-x}Ti_xNi$ ($0.05 \le x \le 0.5$) alloy ingots were prepared with constituents (Zr 99.0%, Ni 99.9% and Ti 99.0% purities) by arc-melting in an Ar atmosphere. Before the arc-melting, titanium was melted a couple of times to remove the residual oxygen in the apparatus. Each alloy ingot was re-melted five times to ensure their homogeneity, and cut to several chips by a wet process machine. Some chips were mechanically pulverized, followed by sieving between 20 and 40 μm in diameter, others were polished to analyze their crystal structure.

The crystal structures of the $Zr_{1-x}Ti_xNi$ ($0.05 \le x \le 0.5$) powders was analyzed by X-ray diffractometry (XRD, Rigaku, RINT-2000) using CuKα radiation ($\lambda = 0.1541$ nm, 40 kV, 20 mA).

Electrochemical measurements of the $Zr_{1-x}Ti_xNi$ ($0.05 \le x \le 0.5$) electrodes

The $Zr_{1-x}Ti_xNi$ ($0.05 \le x \le 0.5$) negative electrodes were prepared as follows. Briefly, the $Zr_{1-x}Ti_xNi$ powder (42.5 mg) was mixed with the Cu powder (5 mg) and 25 μL of 10 mass % polyvinyl alcohol aqueous solution to make a paste. The paste was filled into a porous Ni as a current collector to make a negative electrode. For the activation treatment, the resultant $Zr_{1-x}Ti_xNi$ electrodes were immersed in a boiling 6 M KOH solution for 4 h [11]. The electrolyte solution was a 6 M KOH solution containing 1 M LiOH. The positive and reference electrodes were NiOOH/$Ni(OH)_2$ and Hg/HgO electrodes, respectively.

In the charge–discharge cycle tests, each negative electrode was charged at 100 mA g^{-1} for 5 h and then discharged at 25 mA g^{-1} to a cut off potential of −0.5 V vs. Hg/HgO. After each charging and discharging, the circuit was opened for 10 min. For evaluating high-rate dischargeability, each negative electrode was charged at 100 mA g^{-1} for 5 h and then discharged at difference rates between 25 and 200 mA g^{-1} to −0.5 V vs. Hg/HgO. All electrochemical tests were performed at 333 K.

Results and discussion

Crystal structure of the $Zr_{1-x}Ti_xNi$ ($0.05 \le x \le 0.5$) alloys

Fig. 1(a) shows the XRD spectra of the $Zr_{1-x}Ti_xNi$ ($0.05 \le x \le 0.5$) alloys. The main diffraction peaks in each XRD spectrum were assigned to the *B*33-type orthorhombic structure (ICDD no. 01-072-6477), which was characteristic of ZrNi, suggesting that crystal structure of ZrNi was maintained even when Zr was partially replaced with Ti. Each diffraction peak for the primary phase shifted to the higher angles with an increase in the Ti content. Fig. 1(b) shows the change in the unit cell volume (V_M) of the primary phase as a function of *x* value. The V_M of the primary phase was evaluated to be 0.1326 nm^3 for $x = 0.05$, 0.1308 nm^3 for $x = 0.1$, 0.1282 nm^3 for $x = 0.2$, 0.1263 nm^3 for $x = 0.3$, 0.1229 nm^3 for $x = 0.4$ and 0.1206 nm^3 for $x = 0.5$. For the pristine ZrNi ($x = 0$), V_M was 0.1334 nm^3 [18]. Thus V_M of the primary phase linearly decreased with an increase in the Ti content because Ti was smaller in atomic radius than Zr. This suggests that Ti was uniformly distributed in the primary phase. Moreover, the linear relationship between V_M and *x* agreed with the Vegard's law as follows.

$$V_M = -0.02621x + 0.1334 (0 \le x \le 0.5) \quad (1)$$

For the alloys with $x \le 0.3$, the small diffraction peaks were also observed around 40.1 and 41.3°, which was assigned to Zr_9Ni_{11} (ICDD no. 00-033-0963). According to the Zr-Ni phase diagram [19], Zr_9Ni_{11} is stable more than 1251 K. In this study all the $Zr_{1-x}Ti_xNi$ alloys have Zr/Ni ratios less than 1, so in the arc-melting Zr_9Ni_{11} can partially be precipitated during rapid cooling. The diffraction peaks for Zr_9Ni_{11} also shifted to higher angles with an increase in the Ti content, suggesting that Ti was distributed to both primary and secondary phases.

When x was 0.4, the peaks for Zr_9Ni_{11} disappeared, as shown in Fig. 1. In the Zr-Ti binary phase diagram of the $Zr_{1-x}Ti_xNi$ ($x \le 0.5$) alloys simulated with the Thermo-calc (data base: SSOL5, Thermo-calc software AB), the melting points of the alloys with $x \ge 0.4$ were less than 1153 K, although the melting point of Zr_9Ni_{11} was 1254 K. In the arc-melting method, Zr_9Ni_{11} cannot be precipitated during rapid cooling. Moreover, in the XRD pattern of the alloy with $x = 0.5$, a diffraction peak assigned to $Ti_{0.6}Zr_{0.4}Ni$ (ICDD no. 00-050-1148) was observed. In the simulated Zr-Ti binary phase diagram, the TiNi phase was firstly precipitated at 1075 K, and then ZrNi was also precipitated at 1029 K, suggesting the formation of Zr-contained TiNi phase.

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