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Charge–discharge performance of Cr-substituted V-based hydrogen storage alloy negative electrodes for use in nickel-metal hydride batteries

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ABSTRACT

To improve the charge–discharge cycle durability of a $TiV_{2.1}Ni_{0.3}$ alloy negative electrode with a discharge capacity of ~470 mAh g^{-1}, the vanadium constituent was partially substituted with chromium. The $TiV_{2.1-x}Cr_xNi_{0.3}$ ($x = 0.1$–0.4) alloys, which were prepared by arc-melting, were composed of two phases, similar to the $TiV_{2.1}Ni_{0.3}$ alloy. Each constituent was distributed in both phases, and the V and Cr content in the primary phase was higher than that in the secondary phase, although the Ti and Ni content was higher in the secondary phase. The maximum discharge capacity for the $TiV_{2.1-x}Cr_xNi_{0.3}$ ($x = 0.1$–0.4) negative electrodes showed a slight decrease as the x value increased, and their cycle durability was significantly improved due to the effective suppression of the dissolution of V. In particular, the loss of discharge capacity per cycle for the $TiV_{1.7}Cr_{0.4}Ni_{0.3}$ negative electrode was about one-tenth that for the $TiV_{2.1}Ni_{0.3}$ negative electrode. The high-rate dischargeability (HRD) was also greatly improved by increasing the Cr content. At 200 mA g^{-1} the variations of the HRD and the charge transfer resistance (R_{ct}) with the Cr content were similar, while at 400 mA g^{-1} the change in the HRD at a lower Cr content was markedly different from the change in R_{ct}. Moreover, at a lower Cr content the potential at a 50% degree of discharge stagnated at specific discharge currents over 200 mA g^{-1}. These results strongly suggest that hydrogen diffusion in the primary phase served as the main hydrogen reservoir.

1. Introduction

V-based hydrogen storage alloys with a body-centered cubic (BCC) structure as a primary phase have a high volumetric hydrogen storage capacity, and therefore have potential practical applications as negative electrode active materials for nickel-metal hydride batteries and hydrogen reservoirs for fuel cells. A number of papers on V-based alloy hydrogen storage electrodes have been published [1–11]. Initially, TiV_4 alloys were used as the negative electrode active material [1–5]. We have investigated $TiV_{1.4}$, which forms the hydride, $TiV_{1.4}H_{4.6}$ [12], because its hydrogen storage capacity corresponds to a discharge capacity of 1036 mAh g^{-1}, higher than the discharge capacity of TiV_4H_8 (826 mAh g^{-1}). We investigated the effect of Ni-substitution on the electrochemical performance of the $TiV_{1.4}$ alloy, and found that the $TiV_{0.9}Ni_{0.5}$ electrode showed the highest hydrogen storage capacity (hydrogen-to-metal ratio H/M = 1.69 at 0.5 MPa) and discharge capacity (390 mAh g^{-1}) among the $TiV_{1.4-x}Ni_x$ ($0 \le x \le 1$) electrodes [5]. In addition, the $TiV_{0.9}Ni_{0.5}$ alloy was composed of two phases; the primary phase $TiV_{2.1}Ni_{0.3}$ alloy had a much higher hydrogen storage capacity (H/M = 1.99 at 0.5 MPa) and discharge capacity (470 mAh g^{-1}) than the original $TiV_{0.9}Ni_{0.5}$ alloy [13]. However, the $TiV_{2.1}Ni_{0.3}$ alloy exhibited poor charge–discharge cycle durability because of the dissolution of the V constituent in the 6 M KOH electrolyte solution.

In order to suppress the deterioration of the $TiV_{2.1}Ni_{0.3}$ alloy, we modified the surface of the $TiV_{2.1}Ni_{0.3}$ alloy with an amorphous MgNi alloy by using a mechanochemical technique [14,15]. The spectral data on the modified $TiV_{2.1}Ni_{0.3}$ alloy showed that a mutual diffusion layer of the Mg, Ni, Ti and V constituents was formed at the interface between the $TiV_{2.1}Ni_{0.3}$ and MgNi alloys, and played an important role in suppressing the deterioration of the alloy. The surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni or Raney Ni, which was an effective catalyst for hydriding and dehydriding, was also effective in improving the charge–discharge cycle durability [16,17]. Composite particles prepared by ball-milling the $TiV_{2.1}Ni_{0.3}$ alloy with Raney Ni in the presence of a 0.01 M aqueous solution of sodium hypophosphite (NaH_2PO_2) as a reducing agent, showed a maximum discharge capacity of 620 mAh g^{-1}, although the cycle durability was not improved [18]. Bulk modification, such as partial substitution with foreign elements, is another important strategy for improving cycle durability. Chromium can be oxidized to form a passive layer, which confers high corrosion resistance against acidic and basic aqueous solutions. The Cr substitution of some hydrogen storage alloys has been effective in improving their cycle

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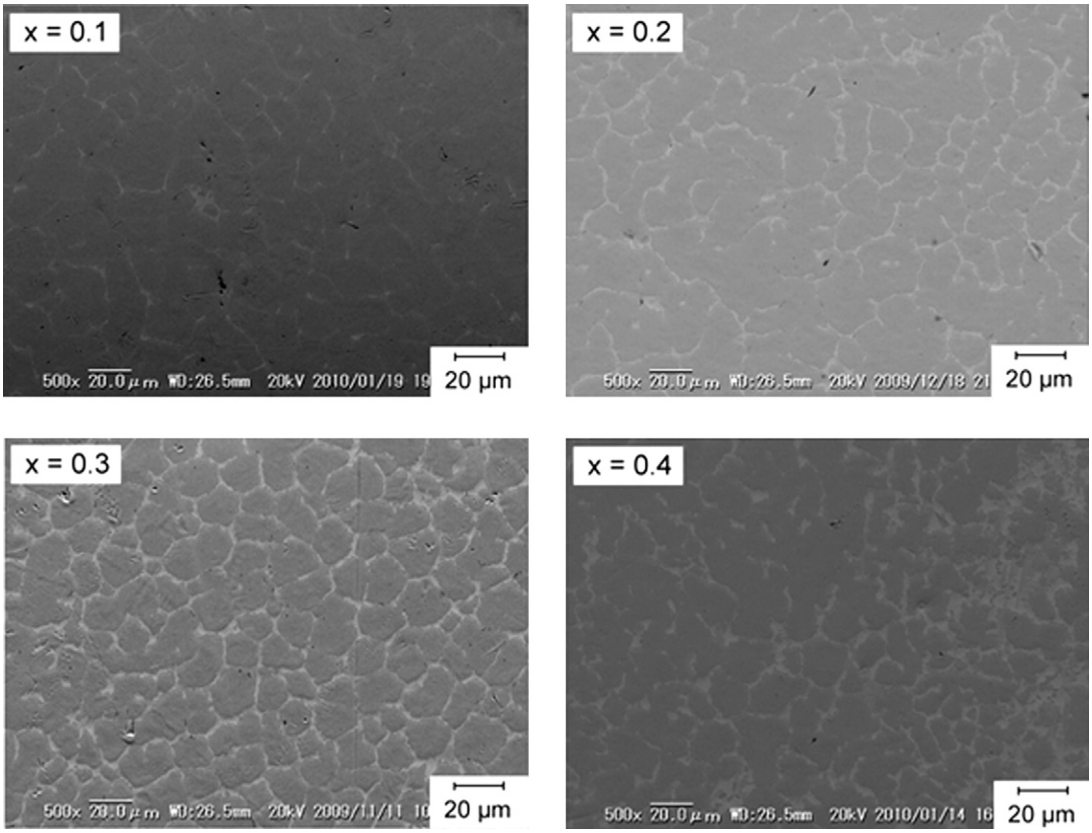

Fig. 1. SEM images of the $TiV_{2.1-x}Cr_xNi_{0.3}$ (x = 0.1–0.4) ingots prepared by arc melting.

durability, although their discharge capacity decreased [19–21]. In this study, we prepared $TiV_{2.1-x}Cr_xNi_{0.3}$ (x = 0.1–0.4) alloys in which Cr was partially substituted for V, in order to improve the charge–discharge cycle durability of the high discharge capacity $TiV_{2.1}Ni_{0.3}$ alloy, which we have previously reported. Characteristics of the battery performance, such as discharge capacity, cycle durability and high-rate dischargeability, were evaluated.

2. Experimental

The $TiV_{2.1-x}Cr_xNi_{0.3}$ (x = 0.1–0.4) alloy ingots were prepared by arc-melting a mixture of Ti, V, Cr and Ni powders under an argon atmosphere. Each alloy ingot was turned over and remelted ten times to ensure its homogeneity. The alloy ingot was then put in a stainless steel reactor tube and broken by the following procedure. Before the introduction of hydrogen, the reactor tube was evacuated at 723 K for 30 min. Hydrogen at a pressure of 0.8 MPa was introduced into the reactor tube and then the tube was cooled to room temperature. These hydriding and dehydriding processes were repeated four times. The coarsely broken alloys were further pulverized with an agate mortar and pestle and sieved to particle sizes of 25–106 μm.

Crystallographic characterization of the $TiV_{2.1-x}Cr_xNi_{0.3}$ (x = 0.1–0.4) alloy ingots was carried out on an X-ray diffractometer (Cu Kα/λ = 1.541 Å, 40 kV, 20 mA, XRD-6100, Shimadzu). The ingots were analyzed by scanning electron microscopy (SEM, VE-9800, Keyence). Before taking SEM images, each alloy ingot was polished with a piece of emery paper (#2000) and then alumina suspensions (0.3 μm, 0.1 μm). The compositions of the two phases in each alloy were simultaneously observed by SEM and by energy dispersive X-ray spectroscopy (EDX). The compositions were evaluated at five randomly selected small areas in each phase and were then averaged. In addition, the composition over the whole alloy ingot was analyzed by low magnification EDX, and was taken as the overall composition.

The mole fraction of both phases in an alloy was evaluated according to the method outlined by Zanowick and Wallence [22]. If the primary phase (composition: $Ti_aV_bNi_cCr_d$ ($a+b+c+d=1$)) and the secondary phase (composition: $Ti_eV_fNi_gCr_h$ ($e+f+g+h=1$)) are present in the mole ratio m:n ($m+n=1$), the content (A–D) of each constituent in the alloy with the overall composition ($Ti_AV_BNi_CCr_D$ ($A+B+C+D=1$)) is expressed as follows:

$$A = ma + ne \tag{1}$$

$$B = mb + nf \tag{2}$$

$$C = mc + ng \tag{3}$$

$$D = md + nh \tag{4}$$

Because A–D and a–h were all experimental values, the four sets of m and n can be evaluated, and their average is taken as the mole fraction of each phase in this study.

The negative electrodes used in this work were prepared by using our previously published procedure [13]. The electrolyte solution was KOH (6 M), and the positive electrode was a $NiOOH/Ni(OH)_2$ electrode. The negative electrodes were charged at 100 mA g^{-1} for 8 h and discharged at 50 mA g^{-1} to the cut-off potential of −0.75 V versus Hg/HgO. After each charging, the circuit was kept open for 10 min. The high-rate dischargeability (HRD) was evaluated over 2 charging and discharging cycles in order to obtain the maximum discharge capacity for each negative electrode. The electrode was subsequently charged at 100 mA g^{-1} for 8 h and discharged at 25–400 mA g^{-1} to the cut-off potential of −0.75 V versus Hg/HgO. AC impedance measurements were carried out at a degree of discharge (DOD) of 50% in the frequency range 20 kHz to 0.01 Hz