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Vanadium-based solid solution alloys with three-dimensional network structure for high capacity metal hydride electrodes

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Abstract

V-based alloys with a 3-D network structure of a TiNi phase provided high-capacity metal hydride electrodes for Ni–MH cells. The network of TiNi phase worked as a micro-current collector and electro-catalyst. It was shown that the micro-structure and chemical composition of the network phase remarkably influenced the electrochemical properties of the V-based alloys. The kinetics of the electrochemical reaction of V_3TiNi_x depended mainly on the volume fraction of the TiNi phase. The cyclic durability was improved by decreasing vanadium content in the TiNi phase by heat-treatment. A network of C14-Laves type phase containing Hf could improve the high rate capability, while a network phase of C14-Laves type phase containing Zr could not. By adding Co, Nb and Ta to a V–Ti–Ni alloy, the durability during charge–discharge cycles was remarkably improved.

Keywords: Vanadium; Discharge capacity; Micro-structure; Hydrogen storage alloy; Metal hydride electrode

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1. Introduction

Metal hydride electrodes with higher discharge capacity than rare-earth metal based alloys for a nickel–metal hydride (Ni–MH) battery have been expected to appear for many years. Vanadium is known to have a much larger hydrogen storage capacity than $LaNi_5$-type (AB_5-type) and Laves-type alloys (AB_2-type) [1]. The V-based alloys were applied to various systems [2], except for the metal hydride electrode because they did not have electrochemical discharge ability in an alkaline electrolyte.

The present authors have developed a new type of V-based electrode materials with higher capacity (420 Ah kg^{-1}) [3] than AB_5-type and AB_2-type electrodes, where a three dimensional (3-D) network of TiNi phase (Fig. 1(a)) [3–6] or Laves-type phase (Ti, A)(Ni, V)$_2$ (A=Hf, Zr) [6–8] was formed to give the alloys the discharge ability. These 3-D micro-network phases were shown to work as both an electro-catalyst and a micro-current collector, as shown schematically in Fig. 1(b). The electrode characteristics of the alloys were controlled by the chemical composition and the micro-structure of the network phase.

The purpose of the present paper is to demonstrate how the discharge capability and cycle life of a V-based electrode could be improved. Different effects of (Ti, A)(Ni, V)$_2$ (A=Zr, Hf) Laves phases and TiNi-based phase on discharge capability will also be discussed.

2. Experimental details

The alloy samples were prepared by arc melting of metal constituents. Some ingots were heat-treated under vacuum for 24 h [9]. Samples were pulverized by hydrogenation at high temperature (≤673 K) under high pressure hydrogen atmosphere (≤3.3 MPa). The metallurgical microstructures were examined by scanning electron microscopy (SEM) and electron probe X-ray microanalysis (EPMA). Pressure–composition isotherms were measured with a Sieverts' apparatus, as described in the previous paper [3].

For the electrochemical evaluations, alloy powder coated with 20 mass% Cu was mixed with 10 mass% FEP binder (Daikin Co. tetrafluoroethylene–hexafluoropropylene copolymer) and the mixture was hot-pressed on nickel mesh [3]. The discharge capacities of the alloys were measured in a half cell at 293 K using an Hg/HgO reference electrode, a 6 M $KOH_{aq.}$ electrolyte and a $Ni(OH)_2$ counter electrode. Charge–discharge cycle tests were conducted by charging at 100 A kg^{-1} and discharging at 50 A kg^{-1} down to −0.75 V vs. Hg/HgO at 293 K.

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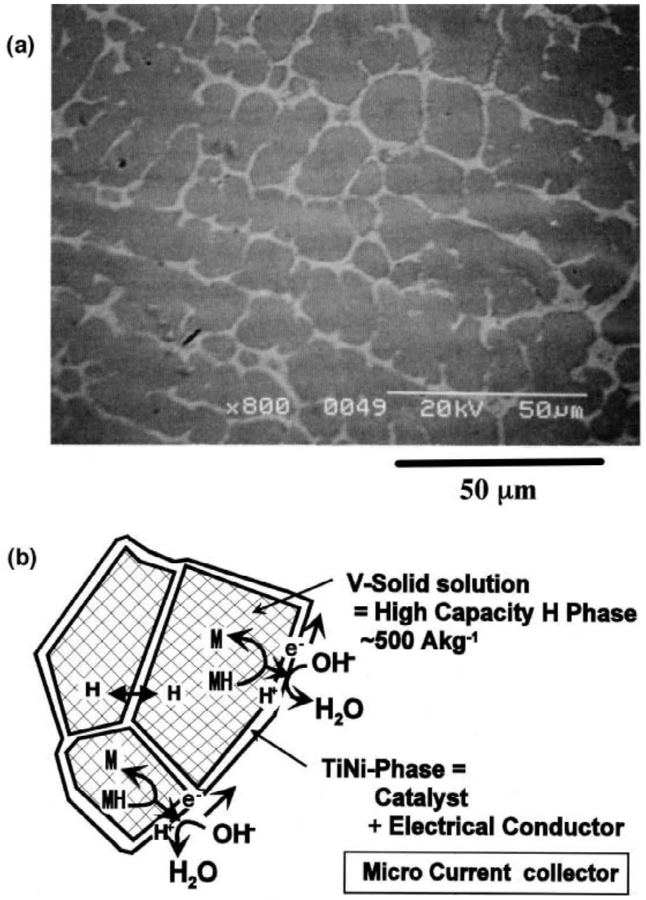

Fig. 1. (a) The cross-section of $V_3TiNi_{0.56}$ consisting of V-solid solution phase (dark gray) and TiNi phase (light gray) and (b) schematic mechanism for electrode reaction on the alloy with micro-current collector.

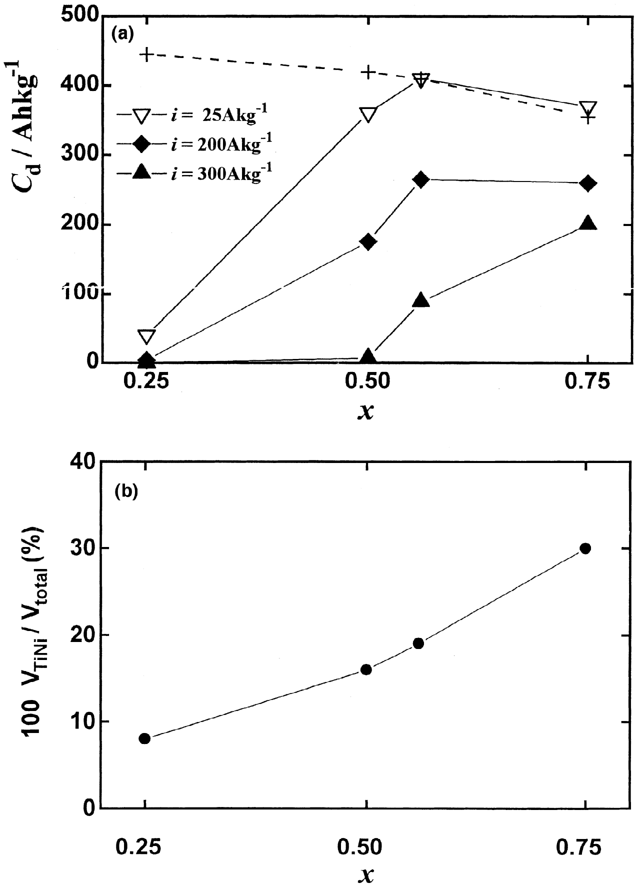

Fig. 2. (a) Plots of discharge capacity C_d for the discharge current density i=25, 200 and 300 A kg^{-1} against the nickel content x for V_3TiNi_x. Dashed line shows the calculated C_d value from pressure–composition isotherms [3]. (b) The volume fraction of the TiNi phase to the alloy against x.

3. Results and discussion

3.1. TiNi phase as a 3-D network phase

The alloys V_3TiNi_x ($x \geq 0.25$) with a 3-D network structure of TiNi phase were used as rechargeable electrodes in KOH solution (Fig. 1). The structure and the chemical composition of the TiNi network as a micro-current collector would influence significantly the kinetic properties and cycle life of the electrodes.

For nickel content x not less than 0.56, the low rate discharge capacity, which is near to the storage capacity of the alloy, depended on the volume fraction of the V main phase (Fig. 2) which would predominantly absorb hydrogen in comparison with the TiNi secondary phase. On the other hand, the high rate discharge capacity depended on the volume fraction of the TiNi secondary phase which worked as the micro-current collector. With decreasing the nickel content ($x \leq 0.5$), the discharge capacity at i=25 A kg^{-1} exhibited a deviation from the values expected from the storage capacity. This deviation would be ascribed to the less volume fraction of the TiNi secondary phase and insufficient network structure.

The V contained in the TiNi secondary phase facilitated the deterioration of the electrodes because it easily dissolved into the KOH solution during charge–discharge cycles. It was successfully decreased by heat-treatment [9], bringing about a significant improvement of the cycle life (Fig. 3). Higher heat-treatment temperature, T_a, than 1173 K, however, degraded the cycle life because the grain size of the V main phase increased and the third phase of Ti_2Ni appeared, which facilitated crack formation in the alloys.

3.2. Laves phase as a 3-D network phase

The addition of M=Hf and Zr to $V_3TiNi_{0.56}M_y$ tended to change the TiNi phase into C14-type Laves phases, such as $TiHf_{0.07}V_{1.09}Ni_{0.29}$, for y=0.046, $TiHf_{0.69}V_{1.09}Ni_{1.15}$, for y=0.24 [6–8] and $TiZr_{0.44}V_{0.67}Ni_{0.88}$ for y=0.24 [6], although the alloy $V_3TiNi_{0.56}Zr_{0.046}$ kept the TiNi phase. Fig. 4 shows the dependence of the discharge capacity C_d on discharge current density i for alloys $V_3TiNi_{0.56}M_y$

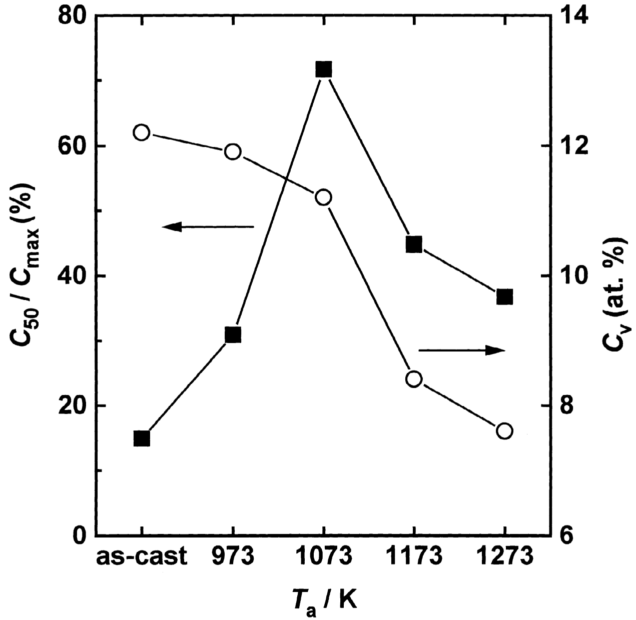

Fig. 3. Plots of ratio of discharge capacity C_{50} after 50 cycles to maximum discharge capacity C_{max} (left hand side) and the vanadium content C_v in the TiNi secondary phase (right hand side) against annealing temperature T_a for $V_3TiNi_{0.56}$.

(M=Zr and Hf, y=0.046, 0.24) in comparison with a rare-earth based alloy of AB_5 [10]. The Hf-containing alloys (y=0.046, 0.24) with (Ti, Hf)(V, Ni)$_2$ Laves-phase network shows better discharge capability than other samples. On the other hand, the Zr-containing alloy (y=0.24) with (Ti, Zr)(V, Ni)$_2$ Laves-phase shows much poorer capability than $V_3TiNi_{0.56}$, in spite of forming almost the same micro-network as the previous alloys. The alloy $V_3TiNi_{0.56}Zr_{0.046}$ containing the TiNi secondary phase shows similar tendency to the original alloy $V_3TiNi_{0.56}$. The network of (Ti, Hf)(V, Ni)$_2$ Laves-phase enhances the high rate capability, but that of (Ti, Zr)(V, Ni)$_2$ Laves-phase degrades it.

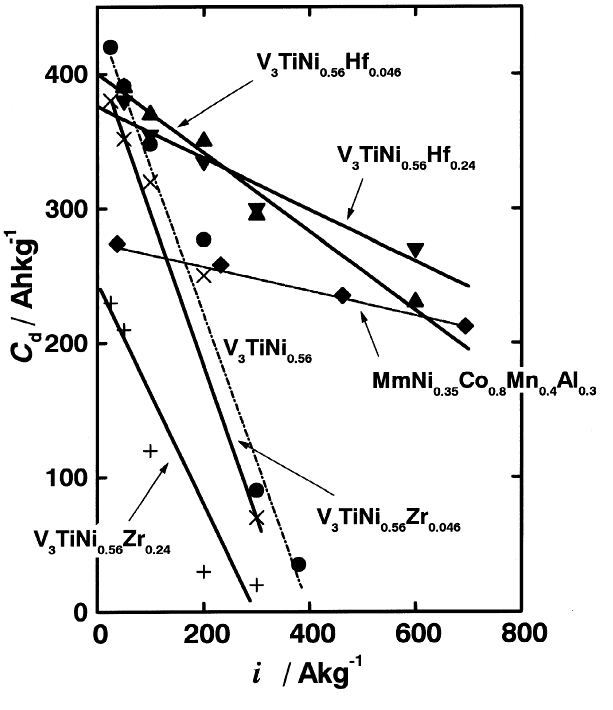

Fig. 4. Plots of the maximum discharge capacity C_d vs. discharge current for $V_3TiNi_{0.56}$, $V_3TiNi_{0.56}M_y$ (M=Zr and Hf, y=0.046, 0.24) and $MmNi_{0.35}Co_{0.8}Mn_{0.4}Al_{0.3}$.

The different behaviors between (Ti, Hf)(V, Ni)$_2$ and (Ti, Zr)(V, Ni)$_2$ Laves-phases would be explained based on the kinetic ability to supply hydrogen onto the reaction surface of the network phase. The (Ti, Hf)(V, Ni)$_2$ phase as the network one could reserve a large amount of hydrogen [8] at room temperature and could quickly supply it onto the reaction surface, while the (Ti, Zr)(V, Ni)$_2$ phase could reserve only a little amount of hydrogen, where the hydrogen should diffuse through the network phase from the V main phase.

3.3. Improvement of the cycle life

The effects of additional elements (M) in $V_3TiNi_{0.56}$ on electrode properties have been systematically investigated to find out the fact that the additions of Co, Nb and Ta were quite effective to improve the cycle life without considerable decrease in the discharge capability [11]. The added Co was distributed mainly in the TiNi secondary phase, by which the mechanical strength and the corrosion resistance of the secondary phase would be improved. Most of the added Nb and Ta were distributed in the main phase of V-solid solution, by which the corrosion resistance of the main phase would be improved. The alloy, including Co, Nb and Ta, ($V_4Nb_{0.047}Ta_{0.047}TiNi_{0.56}Co_{0.14}$), shows better cyclic durability than the original alloy $V_3TiNi_{0.56}$, as shown in Fig. 5.

4. Conclusions

1. The kinetic properties of the electrochemical reaction of V_3TiNi_x were improved by increasing volume fraction of the TiNi secondary phase.
2. The cycle lives of the alloys were improved mainly by decreasing the vanadium content in the TiNi secondary phase, which was done by suitable heat-treatment.
3. The alloys with (Ti, Hf)(V, Ni)$_2$ type Laves-phase network, which could reserve a large amount of hydrogen, showed better discharge capability than other samples. On the other hand, the alloy with (Ti, Zr)(V, Ni)$_2$ type Laves-phase network, which could reserve only a little amount of hydrogen, showed less capability than $V_3TiNi_{0.56}$.
4. The alloy $V_4Nb_{0.047}Ta_{0.047}TiNi_{0.56}Co_{0.14}$ showed much

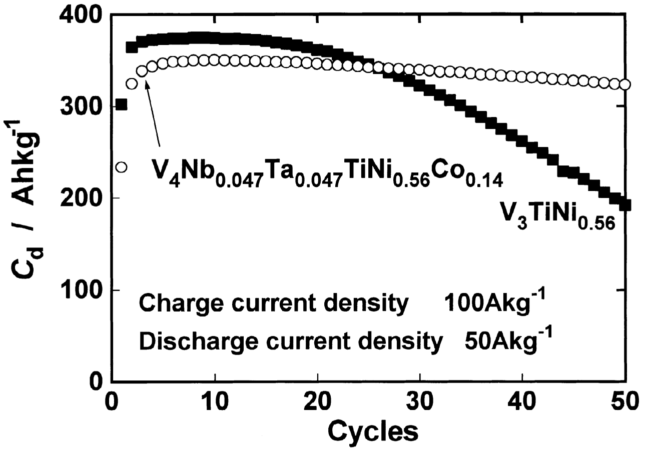

Fig. 5. Capacity decay curve for the $V_4Nb_{0.047}Ta_{0.047}TiNi_{0.56}Co_{0.14}$ electrode in comparison with $V_3TiNi_{0.56}$.

better cyclic durability than $V_3TiNi_{0.56}$, where added Nb and Ta could improve the durability of the V main phase and added Co could improve the durability of TiNi secondary phase.

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