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Influence of carbon on electrode properties of V–Ti–Ni type hydrogen storage alloy

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Abstract

Influences of carbon on microstructure and electrode properties were investigated for battery alloy $V_4TiNi_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}$. With increasing carbon concentration, the cycle-life of charge/discharge became longer. One of main factors that affected the cycle-life was the expansion and reduction of the (Ti,V)-based solid solution phase. Cracks yielded in TiNi phase more easily than in other phases. V-based battery alloys were more hardly pulverized than AB_5 and AB_2 intermetallic compound type materials. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Carbon; Hydrogen storage alloy; Vanadium-based solid solution alloy; Microstructure; Electrochemical PCT

1. Introduction

Vanadium hydrides have been attracting interest because of their high rechargeable capacity of hydrogen at room temperature [1]. Pressure–composition isotherms (PCT) for the reaction between $VH_{\sim 1}$ and $VH_{\sim 2}$ showed a pressure plateau at moderate pressure and temperature [2]. The hydriding properties of vanadium were controlled and improved by alloying with other metals [3]. Such applications as hydrogen compressors, metal hydride heat pumps, hydrogen isotope separation [4] and hydrogen purification [5] were suggested. However, until now the vanadium-based alloys have not been regarded as suitable material for electrochemical applications, because of the excessive corrosion and short cycle-life in electrolyte. Tsukahara and coworkers have developed rechargeable vanadium-based alloys in which a three-dimensional network of a TiNi-based phase [6–9] or a C14 Laves phase [10,11] was found as a microcurrent collector and an electrocatalyst.

A number of investigators [12,13] have shown that dissolved carbon, nitrogen, and oxygen were located at an interstitial site in vanadium metal, and that the solubility and diffusion of hydrogen in vanadium were influenced by the presence of small amounts of these interstitial solutes. The influence of oxygen on microstructure and electrode properties for vanadium-based battery alloys has been reported by Tsukahara et al. [14]. Oxygen showed much less influence on the hydrogen storage capacity for the battery alloy $V_3TiNi_{0.56}Co_{0.14}Nb_{0.047}Ta_{0.047}$ than for the pure vanadium metal, because the titanium formed a $Ti_4(Ni,V)_2O$ type oxygen-containing phase as an inner deoxidizer.

It would be also important to investigate the influence of carbon, which could come from the alloying materials and also could come through other ways during the production process, for the vanadium-based battery alloys. We [15] have found that even though titanium in the alloys worked as a decarbonizer by forming carbide phases, the alloys with 0.1–1.0 wt% carbon lost considerably hydrogen storage ability and discharge capacity, because of the invasion of carbon into the (Ti–V)-based solid solution phase, and that the TiC phase precipitated for alloys containing carbon at more than 0.6 wt%. The aim of the present study is to obtain more detailed information about the effects of carbon on the cycle-life of charge/discharge, volume expansion and reduction, and the electrochemical PCT of the vanadium-based battery alloy.

2. Experimental details

Samples $V_4TiNi_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}$ with 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 wt% carbon were prepared by the same way as reported before in Ref. [15]. The sample electrodes

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were prepared by sandwiching the pellet, which was composed of 25 wt% alloy powder and 75 wt% Cu powder, with a nickel mesh. Charge/discharge cycle tests of each electrode were conducted in a half cell containing 6 M KOH electrolyte at 293 K using an Hg/HgO reference electrode and an $Ni(OH)_2$ counter electrode. The electrode was charged at 100 A kg^{-1} for 5 h, then rested for 30 min and followed by discharging at 100 A kg^{-1} to the cut-off voltage of −0.75 V versus Hg/HgO. Details of the experimental methods regarding metallurgical microstructure examination (scanning electron microscope; SEM) have been described in a previous report [15].

Each electrode sample was withdrawn from the cell after 15, 30, 45 charge/discharge cycles, rinsed with pure water and dried under vacuum at about 300 K. Cross-section of the electrodes were examined by SEM.

Just before measuring the electrochemical PCT curve, several cycles of charge/discharge were carried out to activate the electrode. After that the electrode was charged at 20 A kg^{-1} for 25 h only one time, then the discharge and rest were repeated continuously several times as follows: discharged at 8 A kg^{-1} for 1 h or to the cut off voltage of −0.65 V versus Hg/HgO and then rested for 30 min. The electrochemical PCT curves were drawn from the discharge capacities and the equilibrium electric potentials, the equilibrium electric potentials were detected after 30 min discharge rest.

3. Results and discussion

Discharge capacity versus charge/discharge cycle curves for the samples are plotted in Fig. 1. Discharge capacities decrease with increasing carbon concentration. The first several charge/discharge cycles serve the purpose of activation, the discharge capacities increase with the charge/discharge cycle rather quickly. This suggests that a small amount of TiC does not affect considerably the function of microcurrent collector and catalyst of TiNi phase. Even though the TiC phase hardly absorbs hydrogen [16], the amount of TiC phase in the sample is not large enough to affect the hydrogen storage capacity as showed in Fig. 1. Therefore, the decrease in the measured discharge capacity with increasing carbon concentration is mainly caused by the invasion of carbon into the (Ti,V)-based solid solution phase just like the situation in the PCT measurement [15]. That may be due to the occupation of some interstitial cavities of the alloy by carbon, so the cavities for hydrogen decreases or some other reasons. From the results showed in Fig. 1, it is obvious that with increasing carbon concentration, the decline of discharge capacity on cycling becomes smaller and smaller or the slope of discharge capacity toward charge/discharge cycles becomes flatter, hence the cycle-life of charge/discharge becomes longer. The reason will be discussed as below.

The SEM views for the sample electrodes of $V_4TiNi_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}$ without and with 0.6 wt% carbon, charge/discharge cycled for 30 cycles, are compared in Fig. 2. In Fig. 2(a and b), in the circumference of alloy's particle, a gap in black was observed between the Cu powder in gray and alloy's particle in dark gray. Other sample electrodes show similar SEM views. With increasing carbon concentration, the gap becomes smaller and the number of gaps fewer. The rate of volume expansion caused by absorbing hydrogen is estimated to be about 28% ($MH \rightarrow MH_2$) for pure vanadium, 23% ($MH \rightarrow MH_2$) for $V_{0.8}Ti_{0.2}$ [17], and 9% ($M \rightarrow MH$) for TiNi [18]. The gaps would be made mainly by expansion and reduction of the (Ti,V)-based solid solution phase in alloy's particles during the charge/discharge process. Two alloy samples showed in Fig. 2(a and b) absorbed different contents of hydrogen, so the different expansions were caused. The more hydrogen was absorbed, the stronger expansion was caused and the bigger gaps were made. When bigger gaps

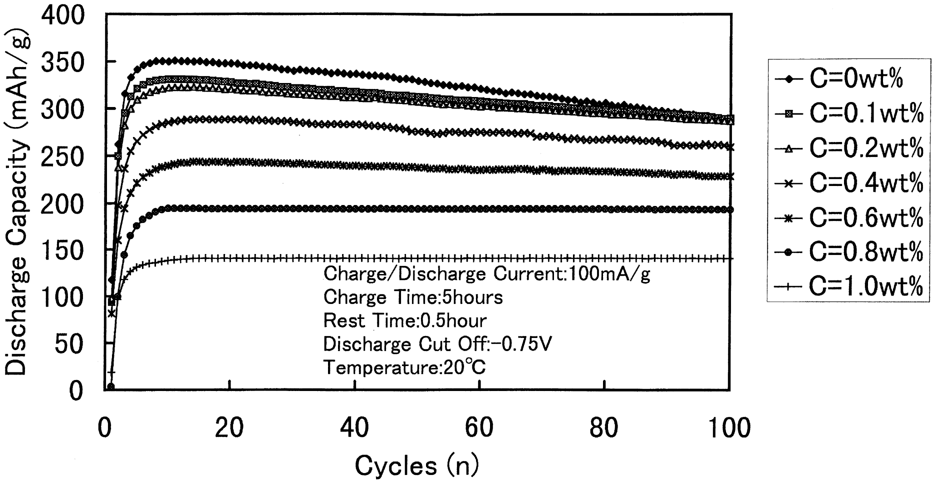

Fig. 1. Relation of discharge capacity and cycle number for $V_4TiNi_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}$ electrode with various carbon concentrations.

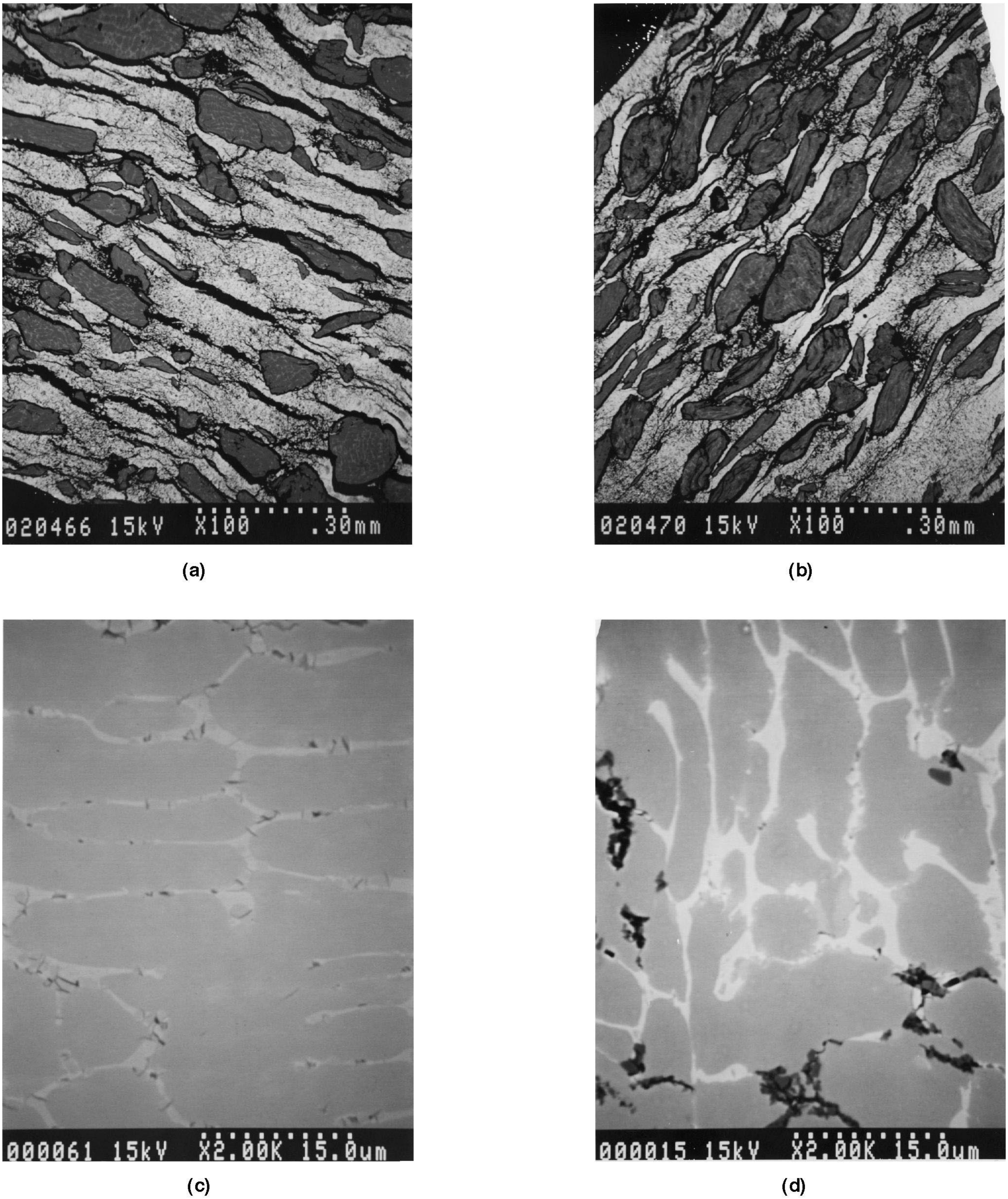

Fig. 2. SEM images of the $V_4TiNi_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}$ electrode without additional carbon (a and c) and with 0.6 wt% carbon (b and d) after 30 charge/discharge cycles with back scattered electrons.

appeared in the sample electrode, the contact between alloy's particle and copper powder or alloy's particles themselves became worse, so bigger decreases of capacity were observed. While with increasing carbon concentration, hydrogen absorbed decreased considerably. So, the expansion and reduction of the (Ti,V)-based solid solution phase is one of the reasons why the cycle-life of charge/discharge becomes longer with increasing carbon concentration.

In Fig. 2(c and d), the gray, bright gray and the black areas respond to the (Ti,V)-based solid solution phase, the TiNi phase and the TiC phase respectively. From Fig. 2(c and d), it can be concluded that cracks yield in TiNi phase more easily than in other phases. That is to say, cracks yield in TiNi phase earlier than in other phases during charge/discharge measurement. The cracking could be ascribed to the difference in expansion ratios between the main phase and the secondary phase. It also can be concluded that the numbers of crack become fewer with increasing carbon concentration [see Fig. 2(c and d)]. With increasing carbon concentration, the hydrogen storage capacity absorbed by the (Ti,V)-based solid solution phase decrease and then the volume expansion become smaller, so the number of cracks decrease too. To obtain powder samples, the vanadium-based battery alloy ingots need to be hydrogenated, while in the case of AB_5 or AB_2 intermetallic compound type materials, the hydrogenation usually is not necessary. So, it could be said that vanadium-based battery alloys are more hardly pulverized than AB_5 and AB_2 intermetallic compound type materials.

The electrochemical PCT curves for $V_4TiNi_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}$ with 0, 0.2, 0.4, 0.6 wt% carbon are showed in Fig. 3. With increasing carbon concentration, the hydrogen desorption pressure become higher and the rechargeable capacity of hydrogen smaller, the former corresponds to the equilibrium electric potential, the latter the discharge capacity. It agrees with the results of PCT curves reported in Ref. [15]. That the hydrogen desorption pressure become higher could be explained as follows: with increasing carbon concentration, more TiC formed and the concentration of Ti in the (Ti,V)-based solid solution phase decreased and then the lattice constant of (Ti,V)-based solid solution phase reduced, because the radius of the Ti atom is larger than that of vanadium. For example, by means of X-ray powder diffraction analysis, the following result was obtained, i.e., the lattice constant of (Ti,V)-based solid solution phase reduced from 3.045 to 3.020 Å, when the concentration of carbon changed from 0 to 0.1 wt%. According to the experience rule in which crystal cell volume and hydrogen equilibrium pressure are included, it is inevitable that the hydrogen desorption pressure, which corresponds to the equilibrium electric potential, become higher with increasing carbon concentration. So the experience rule holds for the vanadium-based battery alloys.

4. Summary

The influence of carbon on microstructure and electrode properties was investigated for the alloy $V_4TiNi_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}$. With increasing carbon concentration, the cycle-life of charge/discharge became longer. One of main factors that affected the cycle-life was the expansion and reduction of the (Ti,V)-based solid solution phase. Cracks yielded in TiNi phase more easily than in other phases. Vanadium-based battery alloys were more hardly pulverized than AB_5 and AB_2 intermetallic compound type materials.

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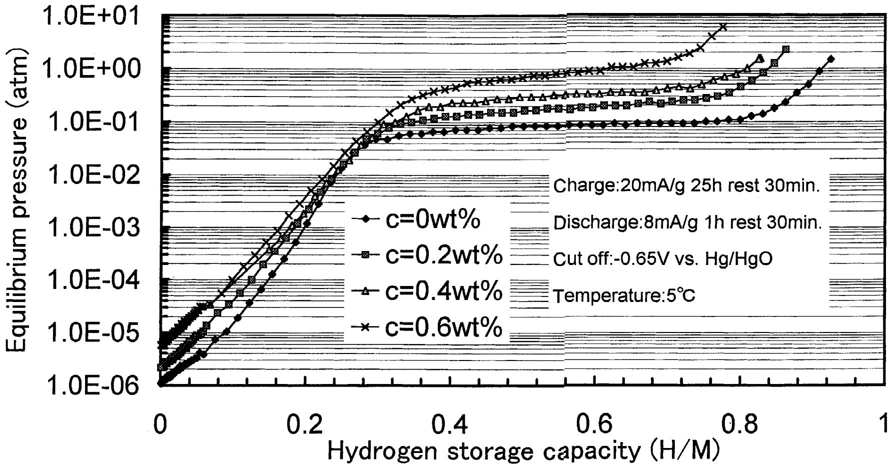

Fig. 3. Electrochemical PC isotherms of $V_4TiNi_{0.65}Co_{0.05}Nb_{0.047}Ta_{0.047}$ electrode with various carbon concentrations.

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